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PRINCIPLES OF FRUIT PRESERVATION

JAM MAKING, CANNING AND DRYING

BY

T. N. MORRIS, M.A.

*University of Cambridge and Department of Scientific and Industrial
Research Low Temperature Research Station*

BEING VOLUME SIX OF A SERIES OF
MONOGRAPHS ON APPLIED CHEMISTRY

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E. HOWARD TRIPP, Ph.D.



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EDITORIAL PREFACE.

IN these days of intensive and extensive research, every worker in science or its applications knows how rapidly the contents of text-books and encyclopædias become out of date ; and those who wish to see new work published know the difficulties which abnormal taxation and high labour costs offer to the realisation of their desire. The one obvious solution of the problem is the publication of monographs that would focus attention upon recent work, or upon new aspects of old work, and upon their theoretical implications. Such books are usually written by experts for other experts in related fields of science, or for the well-educated layman whose thirst for new knowledge has not been quenched by the more sensuous outpourings of the ephemeral press.

It is interesting at times to speculate upon what aspects of our civilisation the future historian will select as the most characteristic of our time. Scientific discoveries and their application to human welfare, we may be sure, will find a place ; and to these many will add the growth of our sense of "values." The value of new work in science varies greatly : the golden grain is always accompanied by chaff, and there is no precious ore without country rock. Owing to the difficulty of assessing the value of work at the time of its production, we find that our scientific periodicals stand in danger of being swamped by the mass of second- and third-rate material that

is thought to be worth publishing, but which posterity will decree would have been better left in manuscript form. It is the first duty of the monograph writer to estimate the value, either actual or potential, of recent work upon the subject of which he writes: he must pick out the plums to save others from the indigestion that follows eating the whole pie. Further, in addition to being accurate, his work must be presented in a form that is both assimilable and attractive; in other words he must show that lucid exposition can be achieved by the use of few words, if they are rightly chosen, and that attractive presentation is attained rather by clear thinking than by superficial display.

The present series of monographs has been designed with these objects and ideals in view. The task which the authors have been set is no easy one; so that should performance occasionally fall short of intention, the critical reader is asked to echo the words of Goethe that "higher aims, even if unfulfilled, are in themselves more valuable than lower aims quite attained."

E. HOWARD TRIPP.

PREFACE.

THIS book has behind it nine years of research and factory experience in the Fruit-Preserving Industry and five years research on the special problems of Fruit-Canning.

As the title indicates, it deals with the scientific principles and control of the various processes involved in the manufacture of jams and fruit jellies, fruit-canning and fruit-drying. For an understanding of these it has been necessary to give some account of the composition of fruits, especially in regard to their contents of acids, sugars and pectin. The manufacture of jams and jellies, in particular, involves a delicate balance between these three classes of substances; hence pectin and the pectin-sugar-acid gel are treated at length, and hitherto unpublished work on this subject by Dr. W. G. Ogg, director of the Macaulay Institute of Soil Research, Aberdeen, has been included. The various methods of preserving fruits for jam-making and canning out of season are also described, and there is an account of the control of the actual manufacturing processes by the works chemist.

In the section on fruit-canning considerable space has been allotted to the problems of can-corrosion, a major source of trouble with certain products, especially in warm climates. The various stages of the canning process are also described and discussed in their proper sequence, and there are chapters

on the standardisation and examination of canned products and on fruit bottling.

The section on fruit-drying deals with recent researches in the U.S.A., Australia and South Africa, both in connection with sun-drying and with artificial dehydration. Space is also given to the subject of prune-drying in France and the drying of grapes in Australia. There are also discussions of the problems connected with the storage and packing of dried fruits and of the general considerations in constructing and working a dehydrating plant.

At the end of the book there are two chapters on subjects common to all the sections. One of these deals with the nature of fruit colours and their behaviour towards metallic salts and other agents of discoloration; the other with the effects of the various manufacturing processes on the vitamins in fruits.

Although the book is mainly designed to assist the chemist and the technical expert, it is hoped that it will also prove useful to the engineer, since for a good many processes the broad outlines of factory requirements are laid down, and, in any case, an understanding of the principles underlying a process can scarcely fail to inspire and guide the construction of the plant necessary for commercial production.

The author's thanks are due to the following: Messrs. Griffin & Co. [London] and Mr. T. Macara, head of the Food Manufacturers' Research Association, for Tables I. and II. respectively; Dr. W. G. Ogg for permission to make free use of his dissertation on the pectic substances of plants; Dr. C. A. McCue, Dean and Director of the University of Delaware Agricultural Experiment Station, for permission to reproduce diagrams from the station's bulletins by Messrs. L. W. Tarr, P. B. Myers and G. L. Baker; the editor of

"Food Manufacture" [published by the Leonard Hill Co., London] for Fig. 11; Dr. W. D. Bigelow, director of the National Cannery Association, U.S.A., for Figs. 12 to 18; Dr. Anderssen of the Union Department of Agriculture, South Africa, for Fig. 28; Drs. P. F. Nichols and A. W. Christie of the University of California for Figs. 29 and 30 [Dr. Nichols kindly lent the engraver's proofs of these]; the editor of the Journal of the Department of Agriculture for Victoria for Fig. 31; the editor of Farming in South Africa for Figs. 32 and 33; the U.S.A. Department of Agriculture for Figs. 34, 35 and 36 and Table XXIII. from Agricultural Bulletin, No. 1335; Professor W. V. Cruess of California University and the McGraw-Hill Book Co. Inc., New York, for Table XXIV. taken from "A Laboratory Manual of Fruit and Vegetable Products," by W. V. Cruess and A. W. Christie; and finally to H.M. Stationery Office for permission to reproduce Figs. 19 to 26 in consideration of a fee of one guinea.

My thanks are also due to Mr. J. M. Bryan, B.Sc., and Dr. E. H. Callow of the Low Temperature Research Station, Cambridge, and Mr. W. G. Greaves, M.A., late of Downing College, Cambridge, for reading the MS. and proofs of the book, and to my assistants, Messrs. A. Fawkes and R. W. Palmer, the photographers of several of the graphs and of the apparatus shown in Fig. 27.

T. N. MORRIS.

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INTRODUCTION.

THE COMPOSITION OF FRUITS.

BEFORE entering upon a discussion of the methods and principles involved in the preservation of fruits, it is necessary to give some general account of their composition.

The main constituent of any fruit is water, which makes up from about 78 to 85 per cent. of the total weight ; other volatile constituents, such as essential oils, esters, etc., are usually relatively negligible in quantity, although important from the point of view of flavour and aroma. The non-volatile matter is made up of sugars, fruit acids, pectin and gums, woody fibre and cellulose, nitrogenous substances, mineral salts and, in a few cases, starch.

TABLE I.

COMPOSITION OF FRUITS (*from Wynter Blyth¹ and H. E. Cox*).

Fruit.	Water.	Nitrogenous Substances.	Free Acid.	Sugar.	Other Non-Nitrogenous Matters.	Woody Fibre.	Ash.
Apple .	83.58	0.39	0.84	7.73	5.17	1.98	0.31
Pear .	83.03	0.36	0.20	8.26	3.54	4.3	0.31
Plum .	81.18	0.78	0.85	6.15	4.92	5.4	0.71
Prune .	84.86	0.40	0.5	3.56	4.68	4.34	0.66
Peaches .	80.03	0.65	0.92	4.48	7.17	6.06	0.69
Apricots .	81.22	0.49	1.16	4.69	6.35	5.27	0.82
Cherries .	80.26	0.62	0.91	10.24	1.17	6.07	0.73
Grapes .	78.17	0.59	0.79	24.36	1.96	3.6	0.53
Strawberry	87.66	1.07	0.93	6.28	0.48	2.32	0.81
Raspberry	86.21	0.53	1.38	3.95	1.54	5.9	0.49
Bilberry .	78.36	0.78	1.66	5.02	0.87	12.29	1.02
Blackberry	86.41	0.51	1.19	4.44	1.76	5.21	0.48
Mulberry	84.71	0.36	1.86	9.19	2.31	.91	0.66
Gooseberry	85.74	0.47	1.42	7.03	1.4	3.52	0.42
Currant .	84.77	0.51	2.15	6.38	0.9	4.57	0.72

TABLE II.
EXTREME AND AVERAGE COMPOSITIONS OF FRUITS (after Macara).

	Insoluble Solids (Fibre, etc.). Per Cent.	Soluble Solids, Per Cent.	Total Solids, Per Cent.	Total Sugars.* Per Cent.	Acid as Crystallised Citric. Per Cent.	Pectin as Crude Calcium Pectate, Per Cent.
GOOSEBERRIES—						
Highest	4.35	11.35	15.25	7.1	3.00	1.19
Lowest	1.7	6.9	9.1	2.0	1.47	0.50
Average (86 samples)	2.61	8.45	11.06	3.51	2.22	0.81†
STRAWBERRIES—						
Highest	3.45	13.6	16.2	8.5	1.74	0.78
Lowest	1.3	5.4	7.3	3.2	0.46	0.36†
Average (47 samples)	2.14	8.98	11.12	5.48	0.93	0.53†
RASPBERRIES—						
Highest	9.2	11.9	20.65	7.85	2.68	0.87
Lowest	4.4	5.4	10.9	1.3	1.23	0.378
Average (54 samples)	6.17	7.98	14.15	3.58	1.73	0.538
RED CURRANTS—						
Highest	7.6	12.65	19.7	6.9	2.95	0.67
Lowest	4.05	9.1	13.75	4.05	2.16	0.44
Average (9 samples)	6.02	10.17	16.19	4.80	2.54	0.58
BLACK CURRANTS—						
Highest	7.9	16.7	22.4	8.25	4.32	1.67
Lowest	4.7	10.0	17.25	2.25	2.70	0.63
Average (20 samples)	5.69	14.25	19.94	6.44	3.48	1.08
CHERRIES (on stone-free fruit)—						
Highest	2.7	14.75	17.45	10.6	1.65	0.40
Lowest	0.95	10.7	12.35	6.9	0.41	0.11
Average (12 samples)	1.88	12.41	14.29	8.33	0.88	0.24

THE COMPOSITION OF FRUITS

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VICTORIA PLUMS (on stone-free fruit)—						
Highest	1.6	15.2	16.65	9.1	2.19	1.07
Lowest	0.9	9.6	10.5	5.9	1.15	0.61
Average (14 samples)	1.13	12.63	13.76	7.43	1.64	0.81
GREEN AND GOLDEN PLUMS (on stone-free fruit)—						
Highest	1.35	11.8	12.7	6.5	1.81	1.02
Lowest	0.85	9.1	9.95	4.5	0.97	0.67
Average (5 samples)	1.03	10.80	11.83	5.69	1.47	0.80
RED AND MISCELLANEOUS PLUMS (on stone-free fruit)—						
Highest	1.7	17.05	18.35	10.25	2.79	1.21
Lowest	0.75	9.35	10.35	3.95	0.54	0.54
Average (15 samples)	1.22	13.10	14.32	7.56	1.74	0.82
GREENGAGES (on stone-free fruit)—						
Highest	1.35	17.25	18.3	11.3	1.44	1.03
Lowest	0.95	10.6	11.75	5.35	1.04	0.86
Average (5 samples)	1.16	14.05	15.21	8.00	1.20	0.95
APPLES—						
Highest	5.95	12.55	18.35	9.75	1.84	1.31
Lowest	1.6	9.5	12.15	4.2	0.52	0.49
Average (28 samples)	2.57	11.70	14.27	7.60	1.11	0.75
DAMSONS (on stone-free fruit)—						
Highest	2.8	22.65	24.95	11.45	3.62	1.52
Lowest	1.25	10.55	12.75	3.9	1.80	0.95
Average (18 samples)	1.96	16.03	17.99	7.53	2.48	1.15
BLACKBERRIES—						
Highest	13.55	10.4	23.0	6.7	1.24	0.85
Lowest	6.6	7.85	14.45	3.3	0.52	0.22
Average (11 samples)	9.64	9.06	18.70	5.10	0.85	0.59

* As invert sugar. † Excluding 3 sulphited samples. § Excluding 10 sulphited samples. || As malic acid.

The proportions in which these constituents occur vary greatly in different fruits, in different varieties of the same fruit, and in the same variety at different stages of ripeness, at different periods and conditions of storage, under different climatic conditions and on different types of soil. Such hereditary and environmental variations have been well demonstrated in the intensive researches on apples which have been carried out in Great Britain under the Department of Scientific and Industrial Research by Kidd and West.² Haynes and Archbold,^{3, 4, 5} Evans,⁶ and others; also some idea as to the variability of other fruits is given in Table II. (from Macara).⁷

In most fruits the natural sugars constitute the greater part of the total solids. The chief of these are sucrose and the reducing sugars fructose and glucose. Taking the apple as an example, it has been found by Evans that the composition of the sugar content of a Bramley's seedling apple in October is as follows:—

Total sugar, 6.64 per cent., of which 2.85 per cent. is sucrose,
4.73 fructose and 1.99 glucose.

These proportions, however, vary considerably with the conditions already mentioned.

The principal fruit acids are citric, malic and tartaric; others which may be present in small quantities are succinic, lactic and oxalic. Thus Franzen and Helwert⁸ give the following analysis for the mixture of acids present in apples: Oxalic 0.001 per cent., succinic 4.22, malic 69.57, citric 24.95 and lactic 1.18. Nelson,⁹ on the other hand, found a much less complicated mixture in American apples, the acid being entirely, or almost entirely, malic. The total acidity may vary from about 1.2 per cent. (reckoned as malic acid) in Bramley's Seedling and Normanton, to 0.191 per cent. in Worcester Pearmain; during storage, the acidity of Bramley's Seedlings has been known to decrease gradually from the normal quantity to about 0.2 per cent.

The acids present in other fruits and other varieties of apples have been determined by Nelson and others as follows :—

TABLE III.
THE ACIDS IN FRUITS.

Kind of Fruit.	Citric Acid. Per Cent.	Malic Acid. Per Cent.	Tartaric Acid. Per Cent.	Observer.
Strawberry . .	90	10	—	E. K. Nelson.
Pineapple . .	87	13	—	"
Red raspberry . .	97	3	—	"
Black raspberry . .	100	—	—	"
Lemons . .	nearly 100	trace	—	"
Grapes (Concord) . .	—	60	40	"
Pomegranate . .	100	—	—	"
Loganberry . .	96	4	—	"
" . .	100	—	—	R. S. Hollingshead. ¹⁰
Cherry . .	—	nearly 100	—	H. Franzen.
Apple (Winesap) . .	trace	nearly 100	—	F. Helwert.
Currant . .	chiefly	some	—	E. K. Nelson.
	citric	malic	—	"
Bartlett pears . .	33	66	—	"
Apple (York Imperial) . .	0	100	—	"
Blueberry . .	nearly 100	trace	—	"
Cranberry . .	80	20	—	"

The predominant acid in blackberries is stated by Nelson to be iso-citric ($\text{HOOC} \cdot \text{CH}_2 \cdot \text{CH}(\text{COOH})\text{CH}(\text{OH})\text{COOH}$) 87 per cent., *L*-malic 13 per cent., and traces of oxalic, succinic and ordinary citric acids.

Variations in total acidity which have been observed by the author in the course of a single season with other fruits in good fresh condition are as follows :—

	Maximum per Cent. as Citric Acid.	Minimum per Cent as Citric Acid.
Gooseberries	2.6	0.85
Strawberries	0.97	0.55
Raspberries	2.5	1.4
Black currants	4.0	2.5
Red currants	2.9	1.7

TABLE IV.

*(Compiled from various sources.) **HYDROGEN-ION CONCENTRATION OF VARIOUS FRUIT JUICES AND
FRUIT SYRUPS.

Kind of Fruit.	p_H of Raw Juice.	p_H of Syrup from Canned Fruit.
Grapes	3.8	—
Lemon	2.55	—
Orange	2.7	—
Peach	4.0	3.39 (in water), 3.65 (in syrup)
Pear	4.2	3.59 (Kieffer), 3.9 (Bartlett)
Tomato	5.05	4.2 (puree), 4.19, 4.23, 4.09
Apple	3.35	3.28, 3.11, 2.88
Gooseberries . .	—	2.78, 3.06, 3.04, 3.0, 3.2
Rhubarb (Champagne)	—	3.3
„ (Victoria) . .	—	3.1
Damsons	—	3.2
Victoria plum . .	—	3.2, 3.21
Greengage . . .	—	3.41
Yellow egg-plum .	—	3.2, 3.3
Canned dried prunes .	—	4.1
Apricots (Australian) .	—	3.73
Cherries (Bigarreau) .	—	4.42, 4.8
„ (Gleneagles) . .	—	4.2, 4.29, 4.1
„ (Frogmore) . .	3.95	—
„ (red sour) . .	—	3.19, 3.35, 3.47
Strawberries . .	3.77	3.49, 3.75, 3.39, 3.44
Raspberry (red) . .	—	3.1, 3.3, 3.3
„ (black)	—	3.69, 3.59
Red currant . . .	—	3.0
Black currant . .	—	3.28
Loganberries . . .	—	3.1
Grapefruit	—	3.3
Blackberries . . .	—	3.56, 3.23, 3.38
Quince	3.2	—
Plum	3.6	—

* Chiefly from W. D. Bigelow and P. H. Cathcart,¹¹ "Relation of Processing to the Acidity of Canned Foods"; some figures are from F. Hirst,¹² of the Chipping Campden Research Station, and others from the author's own measurements.

The total acidity of the fruit is, however, no guide to the true acidity or H-ion concentration either of the raw juice or of an extract produced by boiling the fruit in water. This is affected very considerably by buffering-substances such as pectin, organic bases and inorganic salts, and is of the utmost importance in connection with fruit preservation, since it not only has a great influence on the flavour of the fruit or fruit product, but is a determining factor in the formation of the pectin-sugar-acid gel. It also determines the length of time and the temperature at which it is necessary to cook the fruit in order to sterilise it, since all micro-organisms are readily killed by heat at high H-ion concentrations, whereas they may be extremely resistant in media which approach neutrality. Finally, as will be seen later, it has an important influence on the corrosion of tin-plate in canning.

Table IV. gives the H-ion concentration of (a) the raw juices of the principal fruits, (b) the syrup or watery juice from canned fruits. It will be seen that there is not much difference between (a) and (b).

Of the other non-volatile constituents, pectin will receive special mention owing to its importance in the jam and jelly-making industries. The fibre and cellulose form the skeletal structure of the fruit, and the nature of these materials is important in connection with methods of handling, transport and cooking. The mineral salts have, as will be seen later, some influence on the formation of the pectin gel; also, like those obscure substances, the vitamins, they have an important influence on nutrition.

REFERENCES.

COMPOSITION OF FRUITS.

- 1 BLYTH, A. W., and COX, H. E., "Foods, their Composition and Analysis," Griffin & Co. Ltd., London.
- 2 KIDD, F., and WEST, C., Food Investigation Board Annual Reports, 1923 onwards.
"Functional Diseases of Apples in Cold Storage," F.I.B. Special Report No. 23, 1925.

- "Physiology of Fruit, Part I. Respiratory Activity of Apples," *Proc. Roy. Soc.*, 1930, **131B**, 93.
- 3 HAYNES, D., and ARCHBOLD, H. K., "Chemical Studies in the Physiology of Apples," *Ann. Bot.*, 1928, **42**, 965.
 - 4 HAYNES, D., "Chemical Studies in the Physiology of Apples," *ibid.*, 1925, **39**, 77.
 - 5 ARCHBOLD, H. K., "Chemical Studies in the Physiology of Apples," *ibid.*, 1928, **42**, 29; *ibid.*, 1928, **42**, 541.
 - 6 EVANS, D. I., "Chemical Studies in the Physiology of Apples," *ibid.*, 1928, **42**, 1.
 - 7 MACARA, T., "The Composition of Fruits," *Analyst*, 1931, **56**, 39.
 - 8 FRANZEN, H., and HELWERT, F., "Über die Chemischen Bestandteile grüner Pflanzen," *Zeitschr. Physiol. Chem.*, 1923, **127**, 14.
 - 9 NELSON, E. K., "The Non-Volatile Acids of the Strawberry, the Pineapple and the Concord Grape," *J. Amer. Chem. Soc.*, 1925, **47**, 1177.
 "The Non-Volatile Acids of the Blackberry," *ibid.*, 1925, **47**, 568.
 "The Non-Volatile Acids of the Quince, Pear, etc.," *ibid.*, 1927, **49**, 1300.
 - 10 HOLLINGSHEAD, R. S., U.S. Dept. Agric., Bull. 773.
 - 11 BIGELOW, W. D., and CATHCART, P. H., "Relation of Processing to the Acidity of Canned Foods," Bull. No. 17L, Research Lab., Nat. Canners' Assoc., Washington, D.C.
 - 12 HIRST, F., and ADAM, W. B., Canners' Bulletins, Chipping Campden Research Station.

PART I.
JAMS AND FRUIT JELLIES.

CHAPTER I.

THE PECTIC SUBSTANCES OF PLANTS.

It is now common knowledge that fruits and fruit extracts owe their property of forming jellies when boiled with sugar to the substance known as pectin. This was established by Braconnot (1825-32), who described pectin as "le principe gélatineux des fruits." Since that time a great deal of scientific research on pectin, both from the chemical and biological points of view, has been carried out, and is associated with such names as Frémy, Wiesner, Mangin, Bourquelot and Hérissy, Tschirch and Rosenberg, von Fellenberg, Ehrlich, Goldthwaite, Sucharipa, Wilson, Schryver, Haynes and Carré, Tarr, Ogg and many others. Until recently, however, no systematic attempts had been made to collect and correlate the literature scattered over this long period. This has now been accomplished by Ogg¹ (1924), and Branfoot² (*née* Carré) in 1929. A critical summary of the literature on the pectic substances from the biochemical standpoint has also been published by Onslow³ (*Principles of Plant Biochemistry*, Cambridge University Press, 1931).

Ogg and Branfoot, in so far as the résumé of the literature is concerned, necessarily cover a great deal of the same ground. The first, however, makes an original contribution to the study of the pectin-sugar-acid gel; the second lays somewhat more stress on the methods for the estimation of pectin and the changes which the pectic substances undergo in the tissues. Both include in their work a comprehensive list of references to the literature on pectin.

The pectic substances exist in plants as pectose, pectin and pectic acid, and it is necessary here to give some account of

these, their occurrence and recognition in plant tissues, the mode of extracting and preparing pectin, the estimation of pectin in juices or pectinous extracts, and the breakdown of pectic substances by enzymes during the ripening of fruits and by the action of fungi, bacteria or heat. It is also necessary to deal in considerable detail with the pectin-sugar-acid gel.

Pectose.

Pectose or protopectin is the insoluble precursor of pectin into which it is changed by acid hydrolysis; it is associated with cellulose in the cell walls, especially in the region of the middle lamella, of all plant tissues which have not become woody or corky. It is particularly abundant in fleshy roots, fruits and leaves.

Pectose was first recognised in plant tissues by Frémy, who considered that it was an insoluble salt of calcium or potassium which gave rise to free pectin and bases when extracted with acids. Frémy also isolated an insoluble copper compound of pectose by treatment of plant tissues with Schweitzer's reagent, which dissolves away the cellulose. Sucharipa developed this method still further, and claims to have isolated pure protopectin from the copper compounds by treating them with acetic acid.

Since pectose readily yields pectin on being heated with acids, both are believed to contain the same chemical groupings. It has therefore been suggested that it is either an anhydride of pectin or that it is formed by the union of pectin and cellulose with elimination of molecules of water. The latter suggestion was made by von Fellenberg, and has found support in the work of Sucharipa and Carré.

The method of recognising pectose in plant tissues was first developed by Mangin, who employed stains, the most valuable of which is ruthenium red, and by this means the development and disappearance of pectose may be studied microscopically. Branfoot, who has dealt with this subject at considerable length, has described, with the help of numerous illustrations, such changes as they occur in ripening apples.

Pectin.

Pectin is a soluble product formed either by the acid hydrolysis of pectose, or by the action of hydrolysing enzymes formed in the tissues during ripening. Bourquelot and Hérissy have produced it from pectose by the action of an enzyme which they isolated from the fungus *Aspergillus niger*.

Pectin was first recognised by Braconnot (1825), who extracted it from many fruits and also from carrots and Jerusalem artichokes. This writer described it as a substance soluble in water, giving an opaque, mucilaginous, neutral solution which was unaffected by the addition of mineral acids or calcium chloride. He also found that it was precipitated by alcohol as an insoluble jelly, and that, if the aqueous solution was made alkaline, subsequent addition of mineral acid produced pectic acid. Frémy confirmed the findings of Braconnot, but showed that pectin was precipitated from aqueous solutions by the addition of nearly saturated solutions of magnesium sulphate, ammonium sulphate and basic lead acetate.

Physically, pectin has been classed as a reversible colloid of the lyophilic type. Von Fellenberg found that it was coagulated by alcohol, copper sulphate, basic and neutral lead acetates, but not by silver nitrate, mercuric chloride, zinc sulphate, magnesium chloride, calcium chloride and sodium chloride. Von Fellenberg, Ehrlich and others also investigated the composition of pectin, with the result that it is now regarded as a methyl ester of pectic acid, containing, as a maximum, eight methoxyl groups per molecule. The conversion of pectin to pectic acid consists in the replacement, in stages, of these methoxyl groups by carboxyl groups with liberation of methyl alcohol. This is brought about by the action of an enzyme (pectinase) during the ripening of fruits, by prolonged heating with acids, and by saponification with alkalis and subsequent addition of acid.

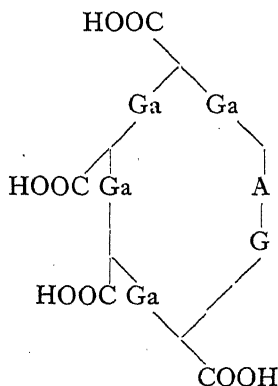
The determination of an empirical formula for pectin is complicated by the difficulty of preparing the substance in a

pure state, and of extracting it without causing some decomposition. It is also a fact that pectin from different sources, or even from the same source at different stages of ripeness, may vary considerably. For instance, pectin from beetroots has been found by Ehrlich and Nelson to contain an acetyl group, which, it is suggested, may account for its failure to form the pectin-sugar-acid gel. Von Fellenberg gives the formula $C_{62}H_{96}O_{52}(COOCH_3)_n(COOH)_{8-n}$ as a general formula which includes the whole range from the neutral octo-methyl ester predominating in fruits just mature, to pectic acid in extremely over-ripe or rotting fruits. Branfoot has termed the intermediate bodies, pectinic acids, and has given the formula $C_{39}H_{58}O_{33}$, which may be provisionally accepted for the fully esterified methyl ester or pectin proper. These two formulæ show close agreement in the relative proportions of the different elements present.

Pectic Acid.

Pectic acid is derived from both pectose and pectin either by acid or alkaline hydrolysis or by the action of an enzyme (pectase). Prolonged heating or the further action of enzymes in over-ripe fruit causes the pectic acid to break down.

It was Ehrlich, who, working with beet residues, first discovered that galacturonic acid is the basal unit of all pectic compounds. Onslow considered that the formula for pectic acid first suggested by Nanji, Paton and Ling, but based largely on the results of previous workers like Ehrlich and Fellenberg, is, possibly, the most satisfactory. It represents the molecule of pectic acid as a closed six-membered ring, of which the members are one molecule of anhydro-arabinose, one of anhydrogalactose and four molecules galacturonic anhydride, the four carboxyl groups of the latter being free.



G = Galactose.
 A = Arabinose.
 Ga = Galacturonic Acid.

Norris and Schryver, and Norris and Norman accept this arrangement. The two former regard pectin as having three and the latter four of the carboxyl groups esterified by methyl alcohol.

Summing up the situation, Onslow states that pectic acid is probably an arabino-galacto-tetragalacturonic acid. If this formula is doubled, it differs only a little from that of Fellenberg, who introduces a methyl pentose instead of a galactose molecule. With regard to the fixation of pectin in the cell wall, Onslow suggests either that carboxyl groups of pectic acid are condensed with cellulose or complexes of pectin molecules are rendered insoluble by loose combination with calcium or ferric ions. It seems certain that pectates of calcium or magnesium exist in the cell wall, especially in the middle lamella.

Onslow considered that most of the investigators were probably dealing with the same substance with varying amounts of impurity, depending upon the methods of extraction and treatment. This, however, still remains somewhat doubtful, in view of the difference in the power of pectins * from different sources to form the pectin-sugar-acid gel, and it seems possible that some of the peculiarities observed, as, for instance, the presence of an acetyl group found by Ehrlich, and Nelson and

* Codling and Woodman ⁵ have shown that beet pectin, no matter how prepared, will not form the pectin-sugar-acid gel. The author has also failed in all attempts to form such a gel.

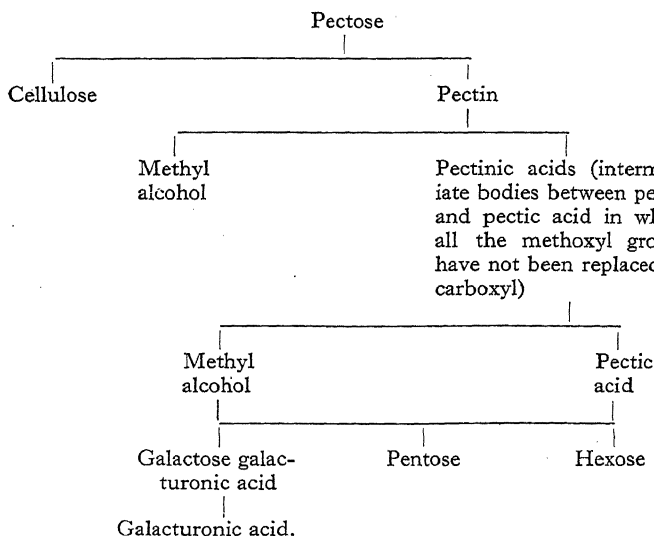
TABLE V.
PECTIC SUBSTANCES (*after Branfoot*).

Substance.	Occurrence.	Composition.	Products of Break-down.	Enzyme causing Breakdown.	Other Agents causing Break-down.
Pectose . . .	Cell walls except where lignified or suberised. Especially abundant in fruits approaching maturity and in fleshy roots	Cellulose plus pectin	Cellulose plus pectin or pectinic acid	Pectosase	Heating with acids or alkalis.
Pectin . . .	Juice of ripe fruits	Octo-methyl ester of pectic acid	Pectic acid and pectates	Pectinase	Prolonged heating with acids. Addition of alkalis.
Pectic acid . . .	Over-ripe fruits	<i>d</i> -galacturonic acid, galactose, arabinose	Reducing sugars	Pectase	Prolonged heating with acids or alkalis.

Mottern,⁴ in beet pectin may represent genuine differences in composition. The changes which pectic substances are liable to undergo are briefly summarised in Table V.

Branfoot has also summarised the changes graphically, as in Table VI.

TABLE VI.



Extraction and Preparation of Pectin.

It has already been indicated that pectose, from which pectin is derived, exists in largest quantity in fruits which have attained their maximum size but have not appreciably undergone those changes which are associated with ripening, such as softening of the tissues and increase in sugar-content. It is especially abundant in citrus fruits, such as lemons, bitter oranges and grape-fruit, and in apples, pears, quinces, gooseberries, currants and plums ; it is less abundant in raspberries, strawberries and cherries.

The chief sources for the manufacture of pectin on a commercial scale are the white or albedo of the rinds of citrus

fruits, and the marc or pomace from the cider and perry presses. These materials are perishables, and if not used at once should be dried and extracted at leisure. Dried citrus rinds may yield from 9 to 18 per cent. of pectin, and apple pomace from 8 to 16 per cent. Carré has repeatedly observed that the pectose in plant tissues is extremely variable in its behaviour towards hydrolysing agents, and considers that this variation depends on the number of cellulose groups attached to the molecule. When this number is large, as in unripe fruits, turnips, etc., acid is necessary, and prolonged boiling may be required to bring about hydrolysis, whilst, with material from ripe fruits, heating with water alone may be sufficient.

In preparing pectin from a substance like apple pomace, the material is first leached with cold water in a suitable wooden vat, provided with a perforated bottom, in order to remove sugars and other soluble substances. The washed pomace is either boiled in wooden vats with eight to ten times its dry weight of a 0.2 per cent. solution of citric, lactic or tartaric acids for about half an hour, the period depending to some extent on the ripeness of the fruit, or heated at a lower temperature (85° - 90° C.) for a longer period.* The mass, which should have the consistency of thin porridge, is either pressed in bags of strong fabric by hydraulic presses, or it may be forced by suitable pumps or by pressure of steam into filter presses of the frame and plate type. The solid portion may be worth a second extraction with boiling water or dilute acid as before, and may then either be dried and fed to cattle or used as fuel or manure.

The extract, which will contain from 0.7 to 1 per cent. of

* Myers and Baker⁹ have recently conducted researches on the extraction of pectin from the albedo of lemons. They find that a larger number of jelly units may be obtained at 70° C. with this material than at any other temperature. The optimum conditions, according to these authors, are: temperature 70° C., H-ion concentration 1.45 p_H , and extraction-period 1 hour. The extract contains a complex of pectic substances. For extracting at 100° C., Myers and Baker obtained the best results by adjusting the p_H to 2.15 and boiling for twenty minutes.

pectin, is collected in large wooden vessels and treated * with amylolytic and proteolytic enzymes, extracted from various moulds grown on malted grains and sold in powder form. These are usually most effective at about 50°C. , and can work in a slightly acid medium. Decolorisation and clarification of the extract are accomplished by boiling with decolorising carbons and filtering through frame-presses after mixing with 1 or 2 per cent. † of kieselguhr free from iron. The result is a pale, straw-coloured liquid, flavourless except for a slight acidity, which is concentrated in a vacuum evaporator of the climbing-film or the multiple-effect type until it contains 3-4 per cent. of pectin. The concentrate is a viscous liquid which may be stored indefinitely by filling it into large cans or bottles, sealing and processing at $85^{\circ}\text{-}90^{\circ}\text{C.}$

It is important in all these operations to avoid contamination of the extract with metals like copper or iron which would cause discoloration of the jam or jelly in which the pectin is subsequently to be used.

Pectin can also be obtained in a less bulky form as a powder; for the preparation of this several methods are available, viz. :—

- (i) precipitation from aqueous solution by means of volatile substances like alcohol or acetone,
- (ii) precipitation along with aluminium hydroxide,
- (iii) evaporation,
- (iv) other methods, such as “salting-out” or electrical precipitation, which have not been applied commercially.

* It may be found more convenient to delay this process until after the extract has been decolorised and clarified, but the enzyme is said to render filtration easier.

† Two per cent. is first added in order to coat the filter cloth; after this 1 per cent. may be used until the filter-presses are full of the cake formed by the kieselguhr.

Precipitation.

Precipitation by substances like alcohol and acetone depend for commercial success on the completeness with which the precipitant can be recovered. In the method recommended by Poore, the aqueous solution, which has been concentrated at low temperature to a thick paste containing 25-30 per cent. of solids, is treated with specially denatured 95 per cent. alcohol containing benzol or ethyl acetate. Sufficient alcohol is added to unite with the water present and form a 60 per cent. alcoholic solution in which the pectin forms a granular, non-gelatinous mass from which the precipitant can be removed by pressure. By using a continuous counter-current washing system, it is claimed that a fairly pure pectin containing only 2 per cent. of ash is obtained with a minimum use of alcohol.

The author has had some success in manufacturing pectin on an experimental scale by using acetone rather than alcohol as a precipitant. Acetone has the advantage of being the easier to rectify owing to its low boiling-point, and there seems no reason why, with suitable plant, its loss should be so large as to render its use uneconomic. In this process the pectinous extract, containing about 1 per cent. of pectin, is mixed with twice its volume of rectified acetone in a closed vessel provided with agitators, and the mixture containing the precipitate forced, by compressed air, through a filter-press with the outlets covered to prevent loss of acetone by evaporation. The liquor from the press, which contains about 60 per cent. of acetone, can be collected and rectified. The acetone in the cake of pectin and in the cloths from the press can also be collected by heating in a water-jacketed oven provided with suitable condensers, and the dried pectin may then be ground, while still brittle, to a fine powder. By using a stronger pectinous extract initially, less acetone is required, but this involves an additional plant for the concentration of the extract which may be as expensive as rectifying the extra quantity of acetone.

Precipitation by aluminium hydroxide * has been described by Jameson, Taylor and Wilson (U.S. Patent No. 1,497,884, 17th June, 1924), and also by Wilson,⁶ and depends on the precipitation of the pectin by the action of a colloid carrying an electric charge opposite to the charge of the colloidal pectin. The method, as described in the patent specification, involves several steps and may be summarised as follows :—

The material from which the pectin is to be extracted is subjected to heat-treatment in order to destroy enzymes which would decompose the pectin, and is also washed with water to remove undesirable soluble impurities. Actual extraction of pectin is carried out by acidified water at 80°-90° C., and the inventors claim that sulphurous acid is exceptionally effective for this purpose.

The extract is made slightly alkaline with ammonia, and sufficient aluminium sulphate is added to render the solution neutral or slightly acidic, these operations being carried out very quickly and with violent agitation. It is also possible to add aluminium hydroxide instead of precipitating it in the extract, or to use a salt like aluminium acetate which is readily hydrolysed, yielding aluminium hydroxide. The precipitate of pectin is pressed, dried and ground to powder, and may be freed from aluminium hydroxide by washing with alcohol containing hydrochloric acid, which removes the aluminium as chloride.

The powder is best brought into solution, when required, by mixing with a strong syrup containing 65-66 per cent. of cane sugar, stirring in boiling water and allowing to stand for a short time. The sugar syrup, not being a solvent for pectin, keeps the latter dispersed, so that it does not form lumps.

* The main details of the process are as given by Wilson, but it appears that some special skill is required to precipitate pectin in this way, and the author has no personal experience of the method.

Evaporation.

Dry, powdered pectin has also been prepared by means of an evaporator of the type used for dried milk. The pectinous extract is sprayed into a heated chamber *in vacuo* at a rate carefully regulated so that dry pectin falls to the bottom of the chamber and the water is carried away as vapour.

Precipitation by Electrolysis.

In the method described by Emmett, for purification of pectin by electrodialysis, it is stated that a layer of mercury served as the cathode of the system, whilst the anode, which dipped into the pectin solution, was of platinum. It was found that it was important to keep to this arrangement if the pectin was to remain in solution, as a reversal of the current caused precipitation. This principle has not been applied commercially, so far as the author is aware, but it would seem to be worthy of further consideration and experiment.

“Salting-Out.”

The salting-out of pectin from solution by saturation with ammonium or magnesium sulphates was first described by Frémy, and an American patent has been granted for its preparation in this way (Doell and Maes).⁷ It is difficult, however, to wash such pectin free from salts, and the method has not much commercial value.

Preparation of Pure Pectin.

In preparing highly purified pectin for experimental work, the method of Bourquelot and Hérissy, with slight modifications, was used by Ogg. Apples at the correct stage of maturity (p. 17) were cored, peeled, sliced and minced. They were then placed under 95 per cent. alcohol, extracted for six hours in a large, specially-constructed apparatus of the Soxhlet type, dried at low temperature, ground to a fine powder, treated in

an autoclave with distilled water at 110° C. for one hour and pressed. To the solution was added twice its volume of alcohol, containing 5 c.c. of concentrated hydrochloric acid per litre. The precipitate was collected, dissolved in warm water and re-precipitated. The final precipitate was washed (a) with alcohol to remove acid, and (b) with ether. It was then dried in a current of warm air and ground to powder. The resulting product contained 5.4 per cent. of moisture and 0.8 per cent. of ash, and on alkaline hydrolysis yielded 11.7 per cent. of methyl alcohol.

Carré and Haynes, and Emmett and Carré recommended the following method : Chloroform and toluene were added to the pectin extracts to keep them sterile, and preliminary purification was effected by filtration through kieselguhr. The pectin was then precipitated with twice its volume of alcohol containing 0.1-0.2 per cent. of hydrochloric acid and allowed to stand for twenty-four hours. The coagulated pectin was filtered on stretched linen or muslin and thoroughly washed by kneading with alcohol; it was then re-dissolved and re-precipitated with alcohol several times, the final precipitation being carried out with absolute alcohol. The precipitate was then transferred to absolute alcohol and afterwards to ether.

These authors state that for further purification the pectin may be re-dissolved and again allowed to stand for some weeks, when further impurities may be deposited. After washing with alcohol and ether the purified pectin was spread out on glass plates and dried in a current of air at ordinary temperatures.

It may be suggested here that treatment of pectinous extracts with an enzyme to remove starch and decolorisation with carbon, prior to filtration through kieselguhr, might have been useful in giving a still purer product. Branfoot states, however, that the pectin prepared as above contained only 0.01-0.03 per cent. of ash, which indicates a high degree of purity. Emmett reduced this amount of ash still further by electrodialysis.

Estimation of Pectin in Pectinous Extracts.

Two main methods are available for the estimation of pectin in pectin sols, viz. : (a) precipitation by alcohol, or better still by acetone, and (b) estimation as calcium pectate by Carré's modification of the Carré-Haynes method.

Precipitation by Alcohol or Acetone.

This method was used by the early workers in estimating pectin, but it has been superseded for more accurate work by the second method, since it has been shown that alcohol may precipitate other substances along with pectin, which are thus estimated as pectin, and also that the percentage of pectin precipitated from a given solution depends upon the concentration of alcohol.

The method is, however, by far the most rapid and convenient for works practice and for comparative tests when dealing with extracts produced in a standard manner from similar materials. It has also the advantage of being indicative of quality as well as quantitative, since an experienced operator can form an opinion as to the jellying quality of the pectinous extract from the nature of the precipitate. If this is gelatinous and collects in a firm mass around the stirring rod, the extract is likely to give a high yield of firm jelly ; if it is broken or flocculent the jelly will be soft and sticky or, possibly, may not form at all. A convenient method used by the author for carrying out rapid estimations of pectin for works purposes is as follows :—

Fifty c.c. of acetone are added to 10 c.c. of pectinous extract, diluted so as to contain about 1 per cent. or less of pectin, in a small beaker. The mixture is stirred and the precipitate kneaded with a glass rod to ensure thorough mixing and precipitation inside the clot, and then filtered through a small, tared sieve of silver or silver-plated copper wire of about 80-100 mesh. The precipitate can be washed or kneaded gently with acetone on the sieve or even collected together and

pressed between filter paper without loss, as it is not at all sticky. It is pressed to a thin flake, replaced on the sieve and dried in an oven at 90° - 100° C. to constant weight. With acetone the drying is complete in fifteen to twenty minutes, and the weight of the precipitate $\times 10$ gives the approximate percentage of pectin in the extract.

It was found by Emmett and Carré (1926) that acidified alcohol precipitates pectin completely at practically all dilutions. The following method based on this fact was therefore devised :

“ The pectin-containing solution was precipitated with four times its volume of alcohol containing the amount of hydrochloric acid required to make the resulting mixture N/10. After standing overnight the precipitate was filtered, washed at once with acidified alcohol, and dissolved off the filter paper with hot water. It was then hydrolysed with sodium hydroxide, and estimated as calcium pectate, the precipitate being washed free from chloride and re-boiled with water three times before being filtered through a Gooch crucible and dried at 100° C.”

With acid alcohol the pectin is precipitated from a pectinous extract more completely and with fewer inorganic impurities than with alcohol in neutral solutions. The method still leaves much to be desired, however, and for accurate estimations the following method is recommended by Carré and Haynes :—

“ A quantity of pectin is taken which will yield from 0.02 to 0.03 grams of calcium pectate ; this is neutralised and diluted so that after the addition of all reagents the total volume is about 500 c.c. 100 c.c. of N/100 sodium hydroxide are added, and the mixture is allowed to stand at least an hour, but preferably overnight, in order to ensure ready flocculation. 50 c.c. of N/1 acetic acid are then added, and after five minutes 50 c.c. of M/1 calcium chloride. The mixture is then allowed to stand for an hour, after which it is boiled for a few minutes and filtered through a large, fluted filter paper. It is then washed free from chloride with boiling water, after which it is washed back into the beaker, boiled and filtered again. It is again tested for chloride and these processes repeated until the

filtrate from the boiled precipitate no longer gives any indication of chloride with silver nitrate." It is then filtered into a small fluted filter from which it can be transferred to a dish, and finally to a Gooch crucible, which has been previously dried at 100° C. The precipitate is dried at 100° C. to constant weight, a process which has been found to require about twelve hours. If the quantity of pectin is increased, the quantities of soda and calcium chloride should be correspondingly increased. If very small quantities of pectin are dealt with the acid and calcium chloride should be reduced.

For estimation of pectin in fruits, Macara¹⁰ uses a slight modification of the method of Carré and Haynes. About 1 lb. of fruit taken from a larger mixed sample was passed through a mincer and 100 or 150 grams weighed out and simmered for one hour with four times its weight of water in a large beaker, with occasional stirring and addition of water to maintain the volume. After cooling to room temperature the mixture was transferred to a measuring cylinder, made up to 500 or 750 c.c. with water and mixed by shaking. The extract was strained through a 120-mesh sieve or filtered through coarse filter paper. For cherries and certain varieties of plums, in which the stones could not be removed clean, a definite weight of the whole fruit was boiled and the stones removed before making up to volume; 50 c.c. of the extract (a larger volume than that recommended by Carré and Haynes) was treated by the Carré-Haynes¹¹ method, except that the time of saponification was shortened to two hours by keeping the volume of extract and alkali at about 100 c.c. After saponification and before precipitation of the pectate, this was diluted to 400 c.c. and filtered on tared filter papers. The results, expressed as percentages of crude calcium pectate on the original fruit (stoneless in the case of plums, etc.), were generally within 0.1 per cent. of those obtained by precipitation with acetone.

REFERENCES.

PECTIC SUBSTANCES OF PLANTS.

- 1 OGG, W. G., "The Pectic Substances of Plants." Dissertation for the Degree of Ph.D. at the University of Cambridge, Cambridge University Library (1924).
- 2 BRANFOOT, M. H., "A Critical and Historical Study of the Pectic Substances of Plants," Dept. Sci. and Ind. Res., Special Report No. 33, 1929. Pub. by H.M. Stationery Office. This work contains an extensive bibliography compiled by Ogg and Branfoot to which reference must be made for the works of many of the writers mentioned in connection with this subject for which reference numbers have not been given.
- 3 ONSLOW, N. W., "Practical Plant Biochemistry," Camb. Univ. Press, 1929.
 "The Principles of Plant Biochemistry," Camb. Univ. Press, 1931 (numerous references).
 ROOKER, W. A., "Fruit Pectin," Avi. Pub. Co., N. York.
- 4 NELSON, E. K., and MOTTERN, H. H., "Pectin," *Fruit Products Journal*, 1931, 10, 138 (numerous references).
- 5 CODLING, A. J., and WOODMAN, H. E., "Sugar-Beet Pulp as a Source of Pectin," *J. Agric. Sci.*, 1929, 19, 701.
- 6 WILSON, C. P., "Manufacture of Pectin," *Ind. and Eng. Chem.*, 1925, 17, 1065.
 "Relation of Chemistry to the Citrus Products Industry," *ibid.*, 1928, 20, 1304.
- 7 DOELL and MAES, U.S. Patent 1,385,525.
- 8 DOUGLAS, R., U.S. Patents 1,082,682, 1,235,666, 1,304,166. (Relating to the extraction of pectin by dilute acids and the clarification of such extracts.)
- 9 MYERS, P. B., and BAKER, G. L., "The Effect of Temperature upon the Extraction of Pectin," Tech. Bull. 168, University of Delaware Agricultural Experiment Station, 1931.
- 10 MACARA, T., "The Composition of Fruits," *Analyst*, 1931, 56, 39.
- 11 CARRÉ, E. M., and HAYNES, D., *Biochem. J.*, 16, 63.

CHAPTER II.

THE PECTIN-SUGAR-ACID GEL.

Historical.

As previously stated, Braconnot was the first to recognise the importance of pectin in the formation of fruit jellies. He also recognised the importance of sugar, and even mentioned the addition of a small amount of acid (hydrochloric or sulphuric acid) "to break up the pectates" when making his jellies.

Subsequently the part played by sugar was lost sight of, and the pectin-sugar-acid gel was confused with the gel of pectic acid formed either by the action of enzymes on a solution of pectin or by the hydrolysis of pectin with alkali and the formation of pectic acid on acidifying. Goldthwaite (1909-10) and Barker (1918) concluded that acid was necessary for gel formation as well as sugar, but von Fellenberg (1918) did not recognise the rôle of acid. He considered that the formation of jellies was bound up with the presence of salts of the alkaline earths or magnesium.*

In 1924-25 an important advance was made when it was definitely established independently, and at about the same time, by Ogg¹ in Great Britain and Tarr² in America, that mixtures of pectin and sugar in solution, free from acid, would not form a gel, and further that the strength and nature of a pectin-sugar-acid gel was dependent on the hydrogen-ion concentration and not on the total acidity.

* Since no jellies have ever been prepared from pectin quite free from ash, it cannot be stated definitely that von Fellenberg was entirely wrong in this contention. The question of the rôle of salts has since been studied by Halliday and Bailey,³ and later by Myers and Baker⁴; all these workers found that the gel is affected by different ions.

THE PECTIN-SUGAR-ACID GEL

Other advances were made by Sucharipa, who concluded that the strength of a pectin gel increased with increase in the methoxyl-content of the pectin. He also drew attention to the fact that pectin is insoluble in a nearly saturated sugar syrup, and succeeded in recovering the pectin from a gel and using it again to form a fresh gel. He assumed, therefore, that formation of the pectin-sugar-acid gel did not involve the conversion of pectin into pectic acid, as had been supposed, but was connected with the insolubility of pectin in the strong sugar syrup.

The Work of Ogg.

One of the chief difficulties in connection with any research on the pectin-sugar-acid gel is to find a satisfactory method for measuring the gel strength. Ogg found the falling sphere viscosimeter most suitable for this work and compared the strength of different gels in terms of their apparent viscosities as calculated by "Stokes'" equation :—

$$v = \frac{2}{9} g r^2 \frac{s - \sigma}{\eta},$$

where v = velocity of fall of the sphere,
 s = density of the sphere,
 r = radius of the sphere,
 σ = density of the medium,
 η = coefficient of viscosity of the medium.

Ordinary steel balls for bearings, which are made with great accuracy in standard sizes, were used as the falling spheres, and the sugar-acid-pectin mixtures were allowed to set under standard conditions (15° C.) in boiling tubes of standard size, fitted with a cork and tube through which the balls were dropped (see Fig. 1). The surfaces of the gels were covered with a few drops of liquid paraffin to prevent the formation of a skin.

Corrections for wall- and end-effects were applied as follows :—

$$9\eta s_1(1 + 2.4x)\left(1 + 3.3 \frac{r}{h}\right) = 2gr^2(s_2 - \sigma)T,$$

where

η = coefficient of viscosity,

s_1 = length (measured of fall),

x = ratio of radius of sphere to that of cylinder,

r = radius of sphere,

h = height of liquid,

s_2 = density of sphere,

σ = density of liquid,

T = time of fall.

By this method it was not possible to distinguish between a gel and a viscous syrup—indeed, there is no hard and fast line—

but the test was considered in conjunction with other physical characters. Thus, a true pectin gel is elastic, can be cut cleanly with a knife, and does not adhere to a glass rod. A syrup of high viscosity, on the other hand, is not elastic, cannot be cut cleanly, and when a glass rod is thrust into it and withdrawn the syrup adheres to it and is pulled out as long threads.

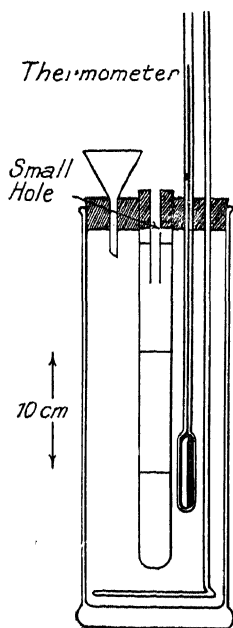
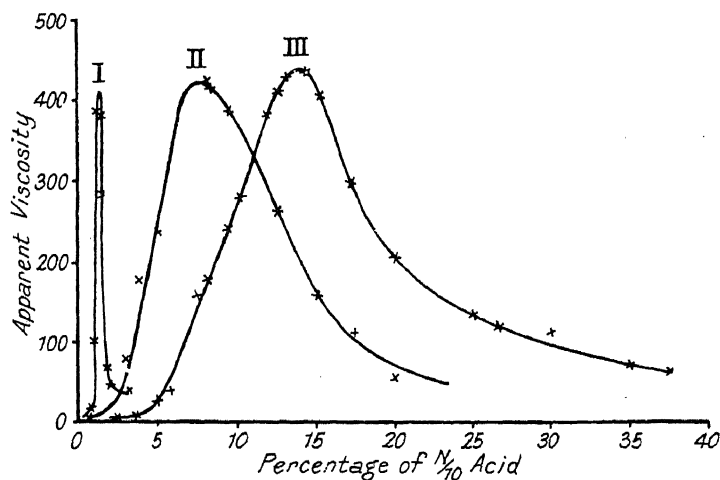


FIG. 1.—Apparatus for measuring the apparent viscosity of the pectin-sugar-acid gel (after Ogg).

Ogg measured the hydrogen-ion concentration in his finished jellies, after the tests for their apparent viscosity had been applied, by means of the quinhydrone electrode, and was able to check his results colorimetrically with a fair degree of accuracy. He thus established a relation between the p_H of the gel and gel strength, as measured by the apparent viscosity, and found that the gel strength was at its maximum at p_H 2.45, but that it fell rapidly on either side of this value, until the

mixture took on the nature of a syrup at about p_H 2.7 on one side and p_H 2.1 on the other. The range within which gel

THE PECTIN-SUGAR-ACID GEL

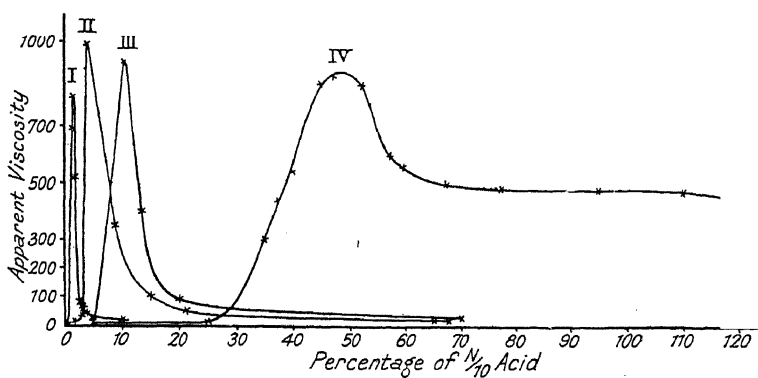


I. Hydrochloric acid. II. Tartaric acid. III. Citric acid.

Percentage of pectin = 0.125.

Percentage of sucrose = 65.

FIG. 2.—The influence of various acids on the firmness of the pectin-sugar-acid gel (cold method) (after Ogg).



I. Hydrochloric acid.

II. Tartaric acid.

III. Citric acid.

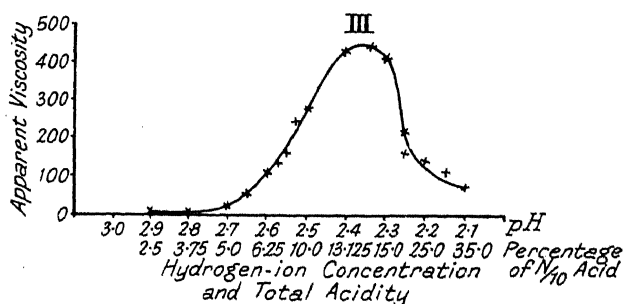
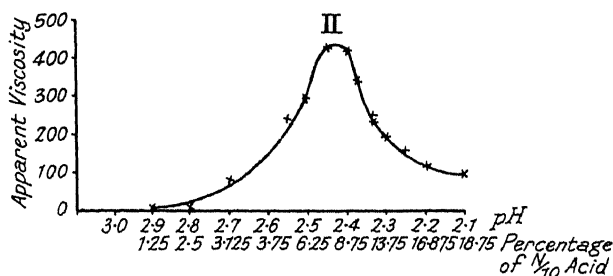
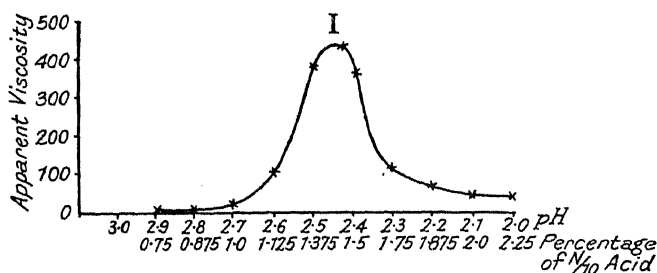
IV. Acetic acid.

Percentage of pectin = 0.25.

Percentage of sucrose = 65.

FIG. 3.—Influence of various acids on the firmness of the pectin-sugar-acid gel (boiling method) (after Ogg).

formation occurred was thus comparatively narrow, and it was noticed that, as the limit was approached on the acid side, there



I. Hydrochloric acid. II. Tartaric acid. III. Citric acid.

Percentage of pectin = 0.125.

Percentage of sucrose = 65.

FIG. 4.—The influence of hydrogen-ion concentration on the firmness of the pectin-sugar-acid gel (after Ogg).

was a tendency towards “weeping” or syneresis, which confirmed a previous observation by Sucharipa. Figs. 2, 3 and 4,

copied from Ogg's monograph, illustrate these findings, and need little or no explanation. It can be seen that the different acid radicles used had very little influence on the maximum strength of the gels, but that this is almost entirely decided by the hydrogen-ion concentration.

Ogg found that gels could be prepared quite readily whether the pectin-sugar-acid mixture was heated or not, and that heating decreased gel strength, and, if prolonged, destroyed the gel altogether, especially at high acidity.

For the preparation of gels in the cold, a solution containing 5 per cent. of pectin was prepared by rubbing up the pow-

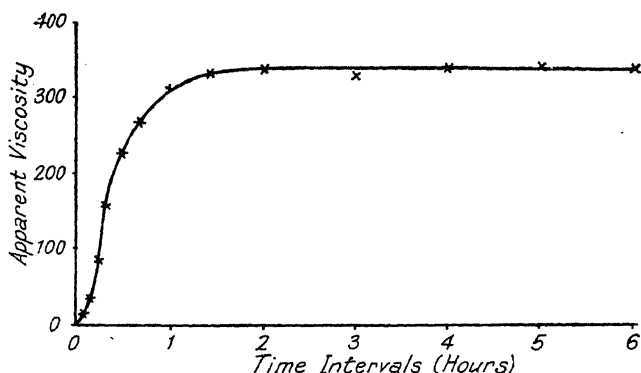


FIG. 5.—The progress of formation of the pectin-sugar-acid gel with time (after Ogg).

dered material (see p. 22) in a mortar with warm water. The quantity of this pectin solution required to give the desired percentage of pectin in the final mixture was weighed out, the weight of standard acid allowed for, and the amount of water available to dissolve the sucrose calculated. The sucrose was weighed into a flask and warmed with distilled water until dissolved. It was then cooled to 30° C., any loss in weight by evaporation made up, and the pectin added. The mixture was shaken thoroughly, poured into three standard boiling-tubes, and at once stirred with a glass rod. A few drops of liquid paraffin were poured on the surface to prevent the formation

of a skin and the tubes allowed to stand in an incubator at 15° C. for eighteen hours.

Several difficulties were encountered in these operations, and it was only possible to carry them out successfully when the concentration of pectin was low (0.125 to 0.25). There was a tendency for air bubbles to become permanently included in the mixture unless great care was exercised, and mechanical agitation was found to have a great effect on the strength of the gel formed. Agitation for one minute was found to give the best results, as seen in Table VII., and was adopted as the standard practice. Table VIII. and Fig. 5 show the progress of gel formation with a mixture of known composition shaken for one minute and allowed to stand in an incubator at $+15^{\circ}$ C.

TABLE VII.

EFFECT OF AGITATION ON GEL FORMATION IN THE COLD
(after Ogg).

Composition of mixture { Pectin, 0.25 per cent. Sucrose, 65 per cent. Acid, 1.5 per cent. of 0.1 N. HCl.		
Duration of Shaking.	Apparent Viscosity of Gel.	Remarks.
0.5 mins.	307	Gel.
1 "	360	"
2 "	325	"
5 "	87	Lumpy gel.

Although the firmness of gel formation, as measured by the apparent viscosity, does not proceed to any extent during the first few minutes, shaking during this period was found to have a marked effect. Ogg therefore concluded that "it would appear that shaking during the early stages broke the bonds that were being formed and prevented the subsequent formation of a firm gel." The influence of mechanical treatment on the viscosity of sols has been noticed by Freundlich and Ishizaka, and on gel formation by Svedberg (1920, Faraday Society,

TABLE VIII.

THE PROGRESS OF THE FORMATION OF THE PECTIN-SUGAR-ACID GEL
FROM THE ABOVE MIXTURE WITH TIME (*after Ogg*).

Time Interval before Measuring the Apparent Viscosity.	Apparent Viscosity.	Remarks.
Immediately	3	No gel.
5 mins.	16	Slight thickening.
10 "	36	"
15 "	88	Gel.
20 "	156	"
30 "	224	"
40 "	264	"
1 hour	312	"
2 hours	335	"
3 "	330	"
4 "	340	"
5 "	348	"
6 "	347	"
12 "	358	"
14 "	366	"

" Discussion on the Physics and Chemistry of Colloids"). This observation has an important bearing on practical jelly-making, since it illustrates the value of filling the jellies into glass as soon as possible after they are made, and avoiding further disturbance until the material has cooled and set.

For making jellies by the hot method, the procedure was similar to the above in the first stages, but after the ingredients were mixed they were boiled together in a flask for five minutes, under a reflux condenser, and with a regulated gas flame. Three tubes were then filled and allowed to set in the incubator at 15° C., as before. Table IX. shows the effect on the gel strength of heating for different periods and for the same period with different amounts of acid. Prolonged heating diminishes the gel strength, especially at high acidity.

Some interesting general observations were made in determining the apparent viscosities of the gels. For instance, it was observed that the smaller spheres in dropping through the gels frequently followed an irregular course. Occasionally they

TABLE IX. (1).

EFFECT OF HEATING FOR DIFFERENT PERIODS ON THE STRENGTH OF THE PECTIN-SUGAR-ACID GEL (*after Ogg*).

Pectin 0.25 per cent. Sucrose 65 " 0.1 N. Citric acid 7.5 "		
Thermal Treatment.	Apparent Viscosity.	Remarks.
Cold	844	Gel.
Just brought to boil .	586	"
Boiled 5 minutes .	524	"
" 10 " .	461	"
" 15 " .	437	"
" 30 " .	401	"
" 60 " .	109	Sticky gel.

TABLE IX. (2).

PERIOD OF HEATING CONSTANT: ACIDITY VARIED.

Pectin 0.25 per cent. Sugar 65 " Acid varied.			
N/10 Hydrochloric Acid. Per Cent.	Apparent Viscosity.		Remarks.
	Cold.	Hot (5 mins. Boiling).	
0.625	5	5	Syrup.
1.25	6	5	"
1.875	960	696	Gel.
2.5	358	224	"
3.75	88	40	Syrupy gel.
5	72	24	"

came almost to a standstill, and then fell rapidly as if they had entered pockets of less viscous material. It was also noticed that in the case of certain mixtures in which there was no appearance of gel formation, e.g. the pectin-sucrose mixture

without acid, the results appeared to obey Stokes' law and the ratios of the rates of fall of the larger spheres to those of the smaller were in this case greater than when gel formation had occurred. From this Ogg suggests that it is possible that a study of the ratio of the rates of fall of spheres of different sizes might throw some fresh light on gel structure.

Ogg noticed, as previously mentioned, that no sucrose-pectin mixtures in solution, without acid, formed gels whether they were heated or not. An important peculiarity, however, of such mixtures was that their viscosity was enormously greater than that of the separate ingredients, so that they might easily be mistaken for gels, and it was suggested that such a mistake might have been made by various workers who had, from time to time, asserted that an acid was not always necessary for gel formation. It was also seen that an increase in the concentration of pectin increased the quantity of acid necessary to bring the hydrogen-ion concentration of the mixture sufficiently high for gel formation to occur. This is of considerable practical importance, and is seen in Table X.

TABLE X.

EFFECT OF INCREASING THE CONCENTRATION OF PECTIN; SUGAR AND ACID CONSTANT.

Ingredients { Sucrose, 65 per cent. 0.1 N. HCl, 3.75 per cent. Pectin, varied.		
Percentage Pectin.	Apparent Viscosity.	Remarks.
0.125	66	Gel.
0.25	216	"
0.5	688	"
1.0 } 1.5 }	Too stiff to measure	Sticky gels.

By increasing the total acidity it is possible to form true gels with the higher concentrations of pectin, and the practical

importance of the experiment lies in the fact that jam manufacturers are sometimes known to add high percentages of pectin to jams or jellies of low acidities with unsatisfactory results. In adding pectin to any product the acidity must always be considered if the best results are to be obtained.

A few experiments were carried out by Ogg to show the influence of the condition of the pectin on the strength of the gel ; but this is a subject on which a great deal more research is required.

Three samples were compared with regard to their jellying properties :—

- (1) Pectin extracted as described (p. 22), and yielding on analysis 0·85 per cent. of ash and 11·7 per cent. of methyl alcohol.
- (2) The same sample re-precipitated several times, dialysed, and yielding 0·5 per cent. of ash and 11 per cent. methyl alcohol.
- (3) Material obtained from apple tissues by boiling with dilute acid after the more easily soluble portion of the pectin had been extracted. This yielded 2·7 per cent. of ash and 7·4 per cent. of methyl alcohol.

The results are set out in Table XI.

It was suggested that in Pectin No. 3 the decrease in firmness was associated with a decrease in the methyl alcohol content, and in Pectin No. 2 with a change in the physical condition or structure of the pectin itself, brought about by the treatment required for purification. There is, in fact, no doubt that the methods employed in extracting and purifying the pectin have an important effect on its power of forming gels.

Observations by Ogg, which confirmed the results of previous workers, concerned the tendency for gels of high acidity to exhibit syneresis, and the fact that gels containing a low percentage of sucrose were tough, while those with a high percentage were soft and easily broken. His original contributions may be briefly summarised as follows :—

- (I) With the low concentrations of pectin (0.125 per cent. and 0.25 per cent.) employed in his experiments, gel formation did not occur, to an appreciable extent, with less than 60 per cent. of sucrose. The concentration of sucrose which gave the maximum strength of gel in a mixture containing 0.125 per cent. of pectin and 1.5 per cent. of N/10 hydrochloric acid was found to be about 67.5 per cent. This agrees closely with the concentration usually found in finished jam, which is largely determined by the "flaking off" test described later.
- (II) Other sugars besides sucrose and also glycerin formed a gel with pectin.
- (III) Moderately firm gels were obtained with as little as 0.125 per cent. of pectin in the mixture, but the firmness depended on the condition of the pectin and varied for different pectins.
- (IV) Gel formation occurred with all the acids employed in the experiments, viz. hydrochloric, sulphuric, nitric, phosphoric, citric, tartaric and acetic. No difference could be observed in the gels obtained with different

TABLE XI.

EFFECT OF DIFFERENT TREATMENT OF PECTIN ON THE GEL STRENGTH.

Per cent. N/10 HCl.	Ingredients { Pectin, 0.125 per cent. Sucrose, 65 per cent. Acid varied.		
	Apparent Viscosity.		
	Pectin 1.	Pectin 2.	Pectin 3.
0.625	3	3	81
1.25	386	3	66
1.875	72	42	30
2.1875	63	27	33
2.5	44	24	24
2.8125	37	12	17

acids, and the maximum strength, as measured by the apparent viscosity, was the same.*

Two per cent. of N/10 hydrochloric, nitric or sulphuric acids produced the same effect as 4.657 per cent. N/10 tartaric acid, 5 per cent. N/10 phosphoric acid, 11.25 per cent. N/10 citric acid, and 55 per cent. N/10 acetic acid.

- (V) Gel formation occurred in the cold, and the effect of heating was to lessen and, in time, to destroy the firmness of the gel, especially at high acidity. Mechanical agitation was also found to have a marked effect on gel firmness.
- (VI) The gel showed evidence of developing nuclei or centres of gelation.
- (VII) Inversion of the sucrose did not affect gel formation, although it was an indication of the p_H of the mixture.

The Work of Tarr.

The work of Tarr and his associates at the University of Delaware, U.S.A., is, in the main, in agreement with that of Ogg. Tarr² made use of a commercial solution of pectin or of a solid pectin obtained by precipitation from such a solution. In his earlier work he had no means of measuring gel strength but merely described his gels as "soft," "tender," "tough," "firm," "good," etc. Also, in all his work measurements of the hydrogen-ion concentration were carried out on the pectin-acid solution before the addition of sugar, and not on the finished gel. The results indicated, however, that the gel strength was dependent upon hydrogen-ion concentration and not on the total acidity, and that it reached a maximum with a pectin-acid solution in the neighbourhood of p_H 3.1. When the solution was on the acid side of this value there was a ten-

* Ogg apparently regarded the slight differences in the maximum gel strengths which he obtained with different acids as being within the limits of experimental error. These differences are, however, in all probability genuine, since they are confirmed by other workers.

dency towards syneresis, and no jelly could be produced from a solution on the alkaline side of p_H 3.46. Tarr, like Ogg, noticed that pectin in solution had a buffering effect* on the acids used in his experiments, which included sulphuric, phosphoric, tartaric, citric and acetic acids. In his later experiments Tarr devised an instrument for obtaining comparative tests of the strengths of different pectin gels so that his results might be made quantitative. This depended on the air pressure (indicated by a manometer) required to break the surface of a pectin gel by means of a plunger. Also in the early experiments the pectin-sugar-acid mixtures were boiled together in an open pan until a gel was indicated by the manner in which the material flaked off a silver spoon, whereas in the later experiments the desired quantities of pectin and acid were accurately measured into a tared pan to which sufficient distilled water was added to make the final volume of the solution 120 c.c. The mixture was then brought to the boiling-point, 100 grams of sugar added, and the whole boiled down on an electric hot-plate to a definite weight (144 grams), so that the final concentration of sugar was about 69.5 per cent.

The gels were allowed to set in glasses of standard size and shape, but there is no mention of any control of temperature during setting; doubtless, however, some such control was exercised.

Fig. 6 shows the alteration in gel strength with varying concentration of sulphuric, tartaric and citric acids, and Fig. 7 the relation of gel strength to the p_H of the pectin-acid solutions. These curves are of similar type to those of Fig. 4 by Ogg.

Tarr differs slightly from Ogg in finding that the "hydrogen-ion concentration, at which the maximum gel strength was attained, varied according to the particular acid employed,

* The difference between the p_H of a pectin-acid solution and that of the finished gel is also due to the effect of cane sugar in increasing the hydrogen-ion concentration of an acid solution, as observed by Lewis and Corran. This accounts for a part of the difference between the p_H -values obtained by Ogg and Tarr in their experiments.

being the least in the case of citric acid, next greatest in the case of tartaric acid, and greatest of all in the case of sulphuric acid" (see Figs. 6 and 7). This difference may be partly due : (a) to slight differences in the technique of the two workers in preparing the gels, (b) to their different methods of measuring gel strength, (c) to the fact that the pectin used by Tarr contained sufficient ash (4 per cent.) to give a salt effect, whereas

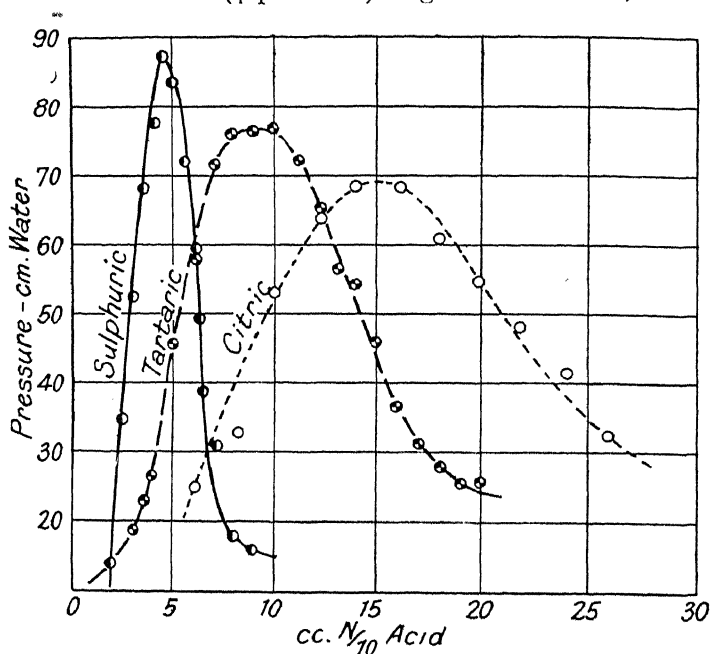


FIG. 6.—Combination curve showing the effect of total acidity on jelly strength (after L. W. Tarr).

that used by Ogg contained only 0.8 per cent., and (d) to the fact that Ogg measured the p_H of the finished gels whilst Tarr measured the p_H of the pectin-acid mixtures before adding the sugar. Of these explanations (c) seems likely to have most weight, but, on the whole, it seems probable that the slight variations due to different acids are genuine (see p. 40, and footnote).

In a pamphlet on the rôle of sugar in jelly formation, Tarr

states that the maximum gel strength was obtained with his mixtures when the final concentration of sugar was 69.5 per cent., although with a purer pectin he obtained the figure 67.6-67.9, which agrees closely with Ogg's figure of 67.5 per cent. The two authorities agree in stating that a low concentration of sugar resulted in a tough gel, and a very high concentration

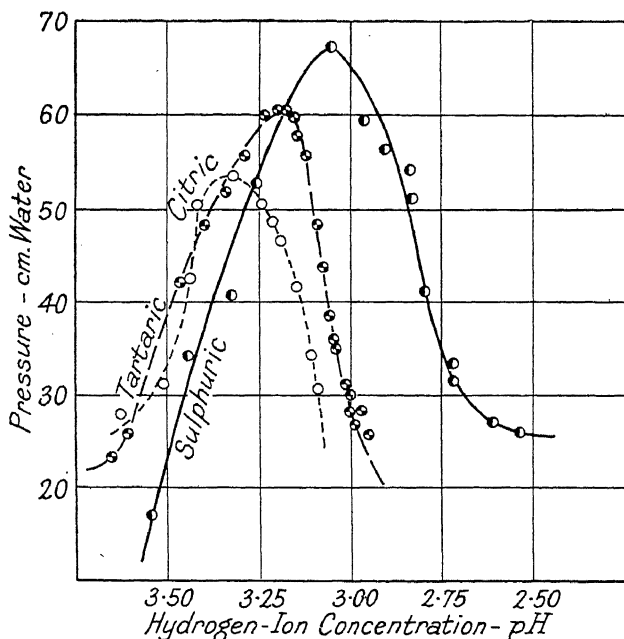


FIG. 7.—Combination curve showing the effect of hydrogen-ion concentration on jelly strength (after L. W. Tarr).

in a weak gel. Also, neither found that inversion of the sugar had any effect on gel strength.

Tarr states that pectin purified by re-precipitation until it contained 1.28 per cent. of ash had a p_H -value in solution of 3.1, and formed a gel with sugar without the addition of acid. It must be pointed out, however, that this result is not in opposition to Ogg's conclusions, since it seems highly probable that the high acidity of this solution was due to acid absorbed from the

acid alcohol used in the precipitation, in spite of the fact that the pectin was well washed.

An important conclusion from his work, to which Tarr draws attention, is the relation between the hydrogen-ion concentration of the acid-pectin solution and the quantity of sugar which must be added to give the maximum gel. When the initial p_H -value of the acid-pectin solution was 3.37, 125 to 130 grams of sugar were required for 125 c.c.; at p_H 3.23, 145 grams of sugar were required, and at p_H 3.1, 170 to 180 grams. The final percentage of sugar, after boiling off water, was the same in all these cases (viz. 69.5 per cent.). Hence it can be seen that the output from a given quantity of pectinous extract bears a distinct relation to its hydrogen-ion concentration. This is interesting in showing how an understanding of the conditions for the formation of the pectin-sugar-acid gel may affect materially the output of jelly from a given quantity of fruit—an important consideration in times of scarcity.

An apparent discrepancy between the results of Ogg and Tarr lies in the fact that, according to the former, the gel strength is seriously impaired, and finally destroyed, by boiling the pectin-sugar-acid mixture, whereas the latter found that this was only the case when the pectin and acid were boiled alone. The sugar had a protective effect on the pectin, and boiling in the presence of sugar for as long as 40 minutes, on the whole, increased the strength of the resulting gel. The author's experience confirms the fact that sugar has a considerable effect in retarding the rate of destruction of pectin in solution by heat, but there is, at the same time, a general feeling, on the part of jam boilers, that the boiling-period should be as short as possible.

Although it is somewhat difficult to reconcile the results of Ogg and Tarr at this point, it should be recognised that their experiments were not strictly comparable. Those of the former involved boiling each mixture of pectin acid and sugar under a reflux condenser, so that, except for inversion, the composition and acidity of the mixture did not alter. The second part of

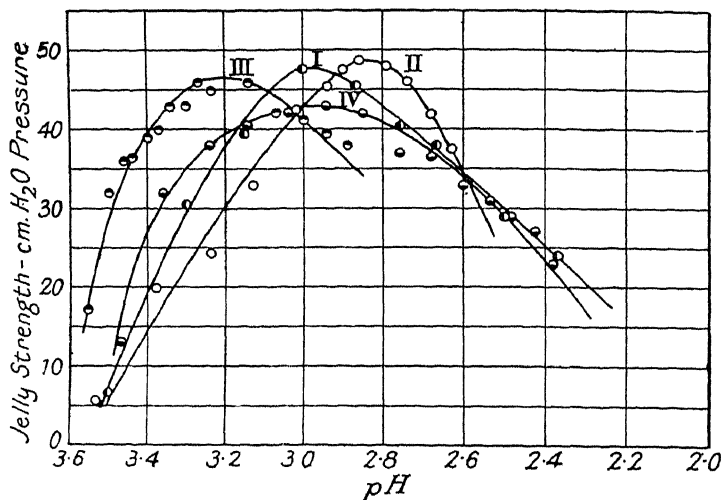
Table IX., which records the effect of increasing the acidity and keeping the period of boiling constant, shows that the greatest relative diminution in gel strength between cold-process and hot-process gels occurred when the acidity was high. In Tarr's experiments the final composition and acidity of each gel was the same, the only difference being that the period of boiling was prolonged in some cases more than in others by the addition of extra water, which had to be boiled away. Hence in this case the initial acidity of the mixtures would be low when it was intended to prolong the boiling period, a fact which might account for the relatively small destruction of pectin. If this view of the matter is correct, it would appear that prolonged boiling is only likely to be serious in the presence of sugar when the initial acidity of the mixture is high ; naturally, however, in economical works' practice the aim should be to cut down the quantity of water to be evaporated as far as is compatible with the sterilisation, cooking and thorough mixing of the ingredients.

The Effect of Salts on the Pectin-Sugar-Acid Gel.

It has been stated by von Fellenberg that jellies could be made by the addition of certain salts to pectin solutions in the absence of acids. Halliday and Bailey³ have also shown that calcium chloride has a favourable effect on gel formation. A systematic investigation of the subject has been made by Myers and Baker,⁴ who suggest that any positive ion may be able to replace partially, if not wholly, the hydrogen ion in gel formation. Myers and Baker, like Tarr, used a commercial pectin solution as a source of pectin which was prepared by precipitating three times with alcohol. The resulting powder contained 3.61 per cent. of ash.

The salts used in these experiments were sodium sulphate, sodium hydrogen tartrate and di-sodium hydrogen citrate. The acids were the same as those used by Tarr, viz. sulphuric, citric and tartaric. The jellies were prepared by Tarr's method, and the jelly strength was measured by means of Tarr's

apparatus. The salts caused the p_H -value of the pectinous solution, from which the maximum gel strength was obtained, to shift slightly (see Figs. 8, 9 and 10). With sodium sulphate this shifting was in the direction of higher acidity, and with sodium hydrogen tartrate and sodium hydrogen citrate it was in the alkaline direction. Whether the p_{II} of the finished jelly was also affected was not determined. In addition to the shifting of the maximum point, the salts, especially the citrate,



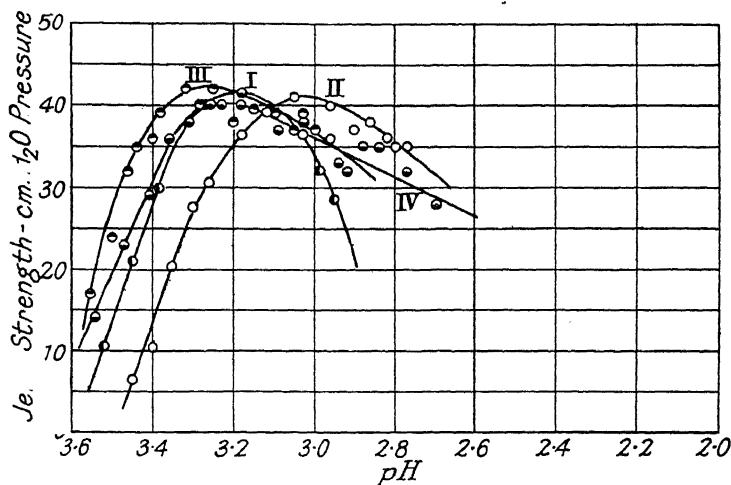
- I. Without added salt.
- II. With 1 gram sodium sulphate.
- III. With 0.5 gram sodium hydrogen tartrate.
- IV. With 0.5 gram di-sodium hydrogen citrate.

FIG. 8.—Curves showing the effect of hydrogen-ion concentration on jelly formation, using sulphuric acid, with and without added salts (after Myers and Baker).

tended to extend very considerably the range of acidity over which a gel could be produced ; this is also seen in Figs. 8, 9 and 10. In other words, the strength of the gel became less sensitive to changes both in hydrogen-ion concentration and normality of acid, especially on the acid side of the maximum. Myers and Baker are of the opinion that the anion of the salt functions mainly as a buffering agent, and may also serve as a peptising agent, if present in sufficient quantity. In their

opinion, syneresis is due to a coagulation of the pectin, resulting from too great a concentration of hydrogen ions, or to hydrogen ions in conjunction with other cations, but not to other cations alone.

Increase in the concentration of the anions is believed to counteract this effect, and so prevents syneresis and consequent weakening of the gel, but Myers and Baker state that the character of a gel is dependent upon the total ionic concentration



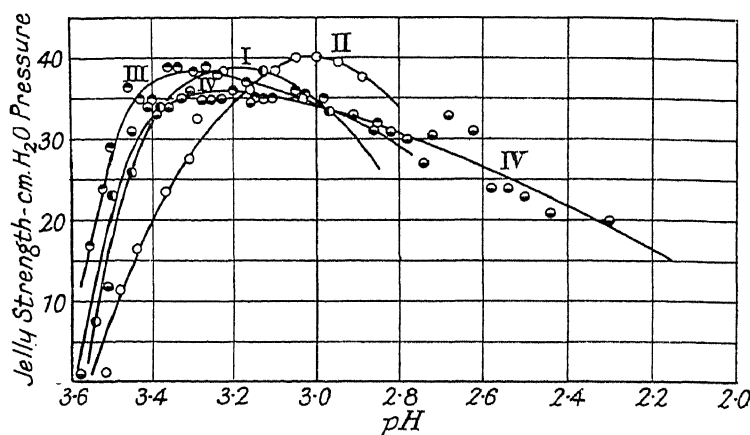
- I. Without added salt.
- II. With 1 gram sodium sulphate.
- III. With 0.5 gram sodium hydrogen tartrate.
- IV. With 0.5 gram di-sodium hydrogen citrate.

FIG. 9.—Curves showing the effect of hydrogen-ion concentration on jelly formation, using tartaric acid, with and without added salts (after Myers and Baker).

of the juice from which it is made. If the ionic concentration is too high after the addition of a salt, syneresis will occur in the gel just as if the salt had not been added.

Myers and Baker also found that an increase in the viscosity of pectin solutions accompanied an increase in gel strength. Some of their arguments in this connection are difficult to follow. For instance, they state that gel strength is a function of the viscosity of the pectin solution from which

the gel is made, and that this relationship is independent of the concentration of the pectin, yet in another portion of their paper they show that viscosity increases with increased concentration of pectin.* It seems that this really means that a pectinous solution may contain a mixture of several pectinous substances, all of which may either be precipitated by alcohol, or as pectate by the calcium-pectate method, and estimated as pectin. Some of these substances give solutions of high, and others of low viscosity, and it is the former which are of greatest



- I. Without added salt.
- II. With 1 gram sodium sulphate.
- III. With 0.5 gram sodium hydrogen tartrate.
- IV. With 0.5 gram di-sodium hydrogen citrate.

FIG. 10.—Curves showing the effect of hydrogen-ion concentration on jelly formation, using citric acid, with and without added salts (after Myers and Baker).

value in producing jellies. Any process, such as prolonged heating or hydrolysis by means of acids or alkalis, in destroying the particular pectinous substance which produces gels, also lowers the viscosity. From this point of view, viscosity

* In a later publication, Myers and Baker state that the viscosity of the pectin solutions was varied both by increasing the concentration of pectin and by regulating the amount of decomposition of the pectin. It was shown that, in both cases, increase in viscosity accompanied increase in gel strength. Results were unreliable at viscosities higher than 20.

measurements would appear to be of some value in judging a pectinous solution. [This interpretation is borne out by later work—see footnote.]

Myers and Baker state that, in precipitating pectin with alcohol, the latter should be run dropwise into the pectin sol, with constant stirring, in order to obtain a pectin of maximum jellying power, and that prolonged boiling of pectic substances with alcohol increases the percentage of water-soluble pectin in the material, but decreases its jellying power. They make the further statement (in which they appear to disagree with Sucharipa and Ogg) that fully methoxylated pectin will not form a jelly, and they believe that the pectinous substance which produces the pectin-sugar-acid gel is intermediate between fully methoxylated and de-methoxylated pectin, but no evidence in support of this view is shown.

The Work of Spencer.

Further work on the formation of pectin gels with sugar has recently been carried out by Spencer,⁶ who claims to have formed them under alkaline as well as under acid conditions. He states that the pectin gel is entirely a precipitation effect and that the acid is *not* essential to jelly formation; also that neutral jellies could also be formed if the solubility of sugar would permit. In his view also, crystallisation limits gel formation on one side of the jelly field and low acid and low sugar on the other. This conclusion is largely based on the finding that gels with alcohol and glycerin were formed at neutrality, as well as in acid and alkaline solutions, but required a maximum concentration of alcohol or glycerin at this point.

Spencer, who prepared his gels in the cold by a method similar to that of Ogg, failed to obtain a falling off in gel strength with increasing acidity. This is in direct contradiction to Ogg's results, of which Spencer could not have been aware, owing to the fact that they were unpublished. It is also opposed to the results of Tarr and Tarr and Baker,⁵ who made their

jellies by the method of evaporation by heat. Spencer attempts to dispose of Tarr's results by assuming that, in the latter's experiments, the falling off in gel strength with increasing acidity was due to hydrolysis of the pectin to pectic acid, which, it is also suggested, may even take place in the cold. No proof is given, however, that such hydrolysis occurred to the extent necessary to bring about the sharp fall in gel strength observed by both Tarr and Ogg with relatively small additions of acid. On the whole, although Spencer's work is of considerable interest, in so far as it suggests a new approach to the subject, more research is required to satisfy all criticisms, and, in any case, for practical purposes the older results still hold good.

One interesting suggestion is made by Spencer to account for the broken or granular condition sometimes encountered in fruit jellies. This is ascribed to the addition of sugar in crystallised form to extracts containing a high percentage of acid and pectin of good jellying quality. It is considered that each sugar crystal becomes a nucleus for gel formation, and that the separate masses of jelly so formed persist during subsequent boiling. Spencer states that, if the sugar is added gradually so as not to cool the mixture to a point at which a gel can form, no granulation occurs. These statements should be verified by using syrup instead of dry sugar.

REFERENCES.

THE PECTIN-SUGAR-ACID GEL.

- 1 OGG, W. G., "Pectin and the Pectin-Sugar-Acid Gel." A Dissertation for the Degree of Ph.D. at the University of Cambridge, Cambridge Univ. Library.
- 2 TARR, L. W., "A Study of the Factors Affecting the Jellying of Fruits," Univ. Delaware Agric. Expt. Sta. Ann. Report, Bull. 133, 14, 1922.
"Fruit Jellies, I. Rôle of Acid," Univ. Delaware Agric. Expt. Sta. Bull. 134, 1923.
"Fruit Jellies, III. Jelly Strength Measurements," *ibid.*, 1926, No. 142.
- 3 HALLIDAY, E. G., and BAILEY, G. R., "Effect of Calcium Chloride on Acid-Sugar-Pectin Gels," *Ind. Eng. Chem.*, 1924, 16, 595.

-
- 4 MYERS, P. B., and BAKER, G. L., "Fruit Jellies, IV. Rôle of Salts," 1926, No. 144, Univ. Delaware Agric. Expt. Sta.
 "Fruit Jellies, V. Rôle of Pectin," 1927, No. 149.
 "Fruit Jellies, VI. Rôle of Pectin," 1929, No. 160.
- 5 TARR, L. W., and BAKER, G. L., "Fruit Jellies, II. Rôle of Sugar," *ibid.*, 1924, No. 136.
- 6 SPENCER, G., "The Formation of Pectin Jellies by Sugar. The Effect of Salts on the Formation of Pectin Jellies. The Relation between Acids and Pectin in Jelly Formation," *J. Phys. Chem.*, 1929, 33, 1987; *ibid.*, 1929, 33, 2012.
- 7 MYERS, P. B., and BAKER, G. L., "Effect of Temperature on the Extraction of Pectin," Univ. Delaware Agric. Expt. Sta. Bull. 168, 1931.

CHAPTER III.

THE MANUFACTURE OF JAMS AND FRUIT JELLIES.

(A) Preliminary Considerations.

A jam, as understood by the manufacturer, is a preparation consisting of whole fruit boiled with sugar, and having a consistency firm enough to meet the demands of confectioners and to withstand the accidents of transport without altering its position in the container or having its surface broken. In other words, jam consists of fruit tissues embedded in a reasonably firm pectin-sugar-acid gel. The only difference between a jam and a fruit jelly is that in the latter the pectin is extracted from the fruit tissues by boiling with water, the extract being separated from all solid materials by pressing in hydraulic presses and filtering either through flannel or iron-free kieselguhr.* It is then mixed with sugar and made into a clear gel.

In principle, therefore, jams and jellies are the same, and, apart from questions of flavour and colour, their method of manufacture turns on the properties of pectin and the laws governing the formation of the pectin-sugar-acid gel.

These underlying principles have received attention in the preceding chapters, and although it is not within the purpose of this book to deal with all the details, mechanical and otherwise, of the manufacture of jams and jellies, it is necessary to

* Bright, sparkling jellies are made by filtering the aqueous extract of the fruit through iron-free kieselguhr (see also Clarification of pectinous extract, on p. 19). This process removes a certain amount of flavour from the product. -

indicate how these principles are, or should be, applied so as to obtain the best results.

The Condition of the Fruit.

Since the content of pectose and pectin is at its maximum in fruit which has attained its maximum size and is just reaching maturity, fruit required for jam or jellies must not be over-ripe, and should be in fresh condition. The processes involved in fermentation, mould growth or over-ripening quickly bring about destruction of pectin and deterioration in colour and flavour, especially in soft fruits. It is true that the pectin can be replaced by artificial means, and in most countries the addition of certain artificial colours is permitted, but it would appear to be bad management to lose the natural colour and pectin of the fruit if these can in any way be preserved. Moreover, loss or impairment of flavour which accompany over-ripeness can never be made good.

This problem of dealing with the fruit while it is in good condition is one of the most difficult with which fruit preservers have to cope, especially in hot weather. Where jam manufacturers have their factories in the country, perhaps surrounded by their own orchards, it is possible, to some extent, to regulate the supply of fruit according to the capacity of the factory and to deal with it in the fresh condition, but, where fruit has to travel long journeys by rail or road, the problem of using it before it has become spoiled or partly spoiled is often acute. In addition to these considerations, there is the fact that the season for any particular fruit is short, so that if a large output is required it is necessary to have very large plant, which may subsequently be idle for long periods. It will also be necessary to be able to draw upon large supplies of labour in the fruit season which will not be required later. It is clear, then, that any method for preserving fruit to prolong the manufacturing period even for a short time is of enormous value. Measures of this kind include cold storage, freezing, heat treatment and the addition of preservatives.

Cold Storage and Freezing.

A cold store, run in conjunction with a fruit-preserving factory, is of great value in forming a reservoir or pool from which fruit can be drawn during the season and thus helps to ensure smooth and regular working. The period during which soft fruits can be kept in cold store at temperatures just above freezing (say 33° - 34° F.) depends, to a great extent, on their condition when they enter it and the kind of vessels in which they are packed. Strawberries, which are among the most perishable of all our fruits, can be kept for over a fortnight at these temperatures when in fresh condition. The author has kept them in chip baskets for nineteen days, but this is exceptional. Probably the length of time for cool storage of this fruit after a journey by road or rail would be considerably less than one week. This is sufficient, however, to ease the situation in times of rush, and the same holds good for other fruits, some of which, like black currants and blackberries, can be held for longer periods.

Soft fruits can also be stored in the frozen condition at temperatures below 14° F. This has been done in barrels* coated internally with special hard wax,† in cans or other suitable metal containers, and in cartons made of waxed cardboard or papier-maché. Raspberries, gooseberries, blackberries, red currants and bilberries can be frozen alone with success. Strawberries, however, tend to develop discoloration and deteriorate in flavour under these conditions; and fruits like plums and cherries turn brown through the action of oxidising enzymes either on thawing or after prolonged exposure to air in the frozen condition. Such fruits must therefore be frozen with sugar or sugar syrup, which, in some way not fully understood, checks the action of the oxidising enzymes. For

* With large containers like barrels it will take at least a week to freeze the contents solid; moreover, barrels should be rolled daily to mix the contents until they are frozen.

† This operation requires some experience; for success the barrels must be quite clean and dry inside.

strawberries, two parts by weight of fruit, with the calyx removed, may be well-mixed with one part of sugar and allowed to stand with occasional careful stirring or rolling of the barrels in a cool place until the sugar has dissolved. The mixture is then frozen and may be held in the frozen condition almost indefinitely. In experiments on these lines at the Low Temperature Research Station,^{1, 2, 3} at Cambridge, and in the U.S.A.,⁴ storage at -20° C. was found to give somewhat better results than at -10° C. over a period of six months, and -10° C. should be regarded as the upper limit for prolonged preservation of strawberries in good condition; -5° C. is definitely too high for this purpose, the resulting product, at this temperature, being dark in colour and of poor flavour. Cherries and plums must be covered with sugar syrup of 30-50 per cent. strength, according to the purpose for which they may be required, and means must be adopted to keep the fruit well under the surface, as those near the surface, or projecting above it, tend to go brown. To prevent browning the fruit must be thawed and cooked as rapidly as possible to destroy enzymes. Strawberries may also be frozen in syrup instead of in dry sugar, with daily rolling until solid, and it is convenient, if they are intended for canning rather than for jam, to freeze them in syrup of canning strength containing about 50-55 per cent. of sugar; but for retailing in the frozen condition a lighter syrup (about 40 per cent.) is recommended in U.S.A. For jam-making it may be suggested that the quantity of fruit (40-60 lb.) sufficient for one boiling of jam should be mixed with 20-30 lb. of sugar in permanent containers of aluminium (or other non-corroding metal) of suitable shape for handling and stacking. Such vessels could be thawed quickly when required, and would save some trouble and calculation, since one difficulty in making jam from fruit frozen in large units is to determine the correct proportions of fruit and syrup "per boil" required to yield a jam of normal and constant fruit content.

The jam made from fruit stored in this way is indistin-

guishable from that made from fresh fruit. Specially sorted fruit, frozen and stored with syrup, also gives excellent results when canned, and in America there is a great and growing demand for the frozen mixture of fruit and sugar or fruit and syrup, which is sold and distributed in that condition in cans or waxed cartons.

The possibility should also be mentioned here of freezing and storing certain fruits quite safely at -10° C. after they have been partly cooked in order to destroy the enzymes which cause them to turn brown or develop unpleasant flavours. This method has proved highly successful in the case of peas and other vegetables, and has also been tried successfully with strawberries,^{2, 3}. Cherries and plums* required for canning should lend themselves to this treatment. It is also claimed in America that effective exclusion of oxygen during storage has the same effect.

The main objection to the storage of fruit in the frozen condition for jam or canning is the capital cost of the cold store. This may, under certain circumstances, e.g. when labour is scarce, be counterbalanced by the smaller plant and staff necessary on the manufacturing side if continuous working over a long period can be secured. There is also the improved quality of the product throughout the year to take into consideration. Many jams and canned goods, finished during one fruit season, lose their good appearance some considerable time before the next arrives, but products freshly made from frozen fruit are as good as those made from fresh fruit, and the quality and quantity of the pectin is unaffected if the freezing is properly carried out. The statement on a label that no preservative has been used may also be found to have a sales value. Important claims in America that a great improvement in texture results from freezing fruits rapidly at temperatures

* By this method strawberries are heated to 80° C. for three minutes in 50-55 per cent. syrup, cooled rapidly and frozen; plums and cherries are boiled gently for four to five minutes, cooled and frozen. Evaporation can be allowed for, if necessary, by adding a little water.

like — 40° C. have been made, although such treatment does not destroy enzymes. These claims have not, so far, been substantiated at Cambridge, and the matter requires further investigation.

Heat Treatment of Fruit.

Fruit, fully prepared for jam-making, may be heated to sterilising temperatures in hermetically sealed containers and stored as partly-cooked fruit pulp. Plums, apples, red and black currants, oranges, apricots, pineapples and peaches may be stored in this way without added sugar. With strawberries and raspberries, however, it is usual to introduce a proportion of the sugar required for making jam and to add the rest later. Large bottles or cans may be filled with pulp and processed, or large stone jars or barrels previously steamed inside, filled through the bung-holes by means of special funnels and bunged tightly, may be used as containers. The barrels should be rolled while still hot to sterilise all parts of the interior. The main objection to barrels and stone jars is the difficulty of sealing them so efficiently as to prevent infection of the contents by yeasts, moulds or bacteria. Moreover, even if the sealing is perfect, some destruction of pectin and deterioration in colour usually results, owing to the fact that the material, being in large bulk, remains hot for a long period. Also with strawberries and raspberries preserved in large bottles or tins with a proportion of sugar there is usually some loss of colour before they come to be used (see p. 105). For these reasons, therefore, the storage of most fruit pulps in this form is practised far less than formerly. The method is still used fairly extensively, however, for apricots and oranges.

Addition of Preservatives for Storing Fruit.

Many of the advantages of cold storage apply also to the use of preservatives, which have the further advantage of involving very little capital outlay. The only preservative which need be

considered for the storage of fruit for jam-making is sulphur dioxide, either in the form of a strong solution of sulphurous acid,* or as calcium or potassium bi-sulphites.† The solution of sulphurous acid is the most convenient for use on a large scale, and when suitably diluted may be added to the sorted and prepared fruit in barrels or other vessels which can be sealed tightly, with precautions to ensure thorough and intimate mixing.‡ According to Barker,§ the preservative fluid should be an aqueous solution containing not less than 0.8 per cent. nor more than 0.1 per cent. of sulphur dioxide. One effect of the sulphur dioxide is to destroy, temporarily and more or less completely, the red colours of fruits such as red plums, strawberries, red currants, raspberries and loganberries. Blue and purple colours are more resistant, and yellows and greens are little affected. There is, however, very little permanent destruction of the colours, which are almost completely restored when the preservative is driven off by boiling; strawberries, however, may require some artificial colouring. Barker states that the sulphur dioxide causes complete stoppage of the enzymic activities in the fruits, although there is a slight loss of pectin in course of time as the result of its slow hydrolysis by the strong mineral acid.§ There is also a slight toughening of the skins of gooseberries, currants and other fruits which so far constitutes a definite drawback to the method.|| In spite of

* Sulphurous acid can be bought as solution containing about 6 per cent. of sulphur dioxide, and such a solution may be used at the rate of about 6 pints for a 40-gallon cask of fruit.

† Williams and Corran⁶ have shown that there was destruction of vitamins with metabisulphites, although they were largely preserved in a sulphured cask. The subject evidently needs further investigation (see p. 227).

‡ This is very important. Also if loss of sulphur dioxide should occur through leakage, this should be made up by the addition of a dilute solution containing 0.1 per cent. of sulphur dioxide.

§ It is doubtful whether all enzymic activity is checked, as the addition of sulphurous acid to fruit juices does not prevent the formation of a gel of pectic acid from the pectic substances present.

|| The author has heard it stated that this toughening can be overcome by cooking the fruit, cooling it and then adding the correct amount of sulphur dioxide. This operation, however, involves extra expense.

minor drawbacks, however, the method is extremely valuable for fruit intended for jam, and has to a very large extent superseded the older method of pulping on account of its greater cheapness, simplicity and reliability. It is permitted by the Board of Trade regulations in Great Britain, provided that the quantity of sulphur dioxide does not exceed 5 grains per pound in fruit pulp offered for sale, or 0.3 grain per pound in the finished jam. Hence sulphurous acid may be regarded as a legitimate preservative and not detrimental to the health of the consumer if present in small quantities; indeed, its use at present holds the field as the simplest and cheapest method of preserving fruit for jam, since barrels of fruit pulp preserved in this way may be stored in the open and require only occasional inspection. At the same time, however, it should be remembered that the policy of the Ministry of Health, as stated in the Final Report of the Departmental Committee on the Use of Preservatives and Colouring Matters in Food (1924), is "that it is undesirable to add to any articles of food any material not of the nature, substance, and quality of the food." In other words, the use of preservatives and colours is definitely discouraged if it can be avoided. At the time when the Report was made, "evidence was given to the effect that preservation by means of cold storage would not be suitable for the fruits mainly concerned." This evidence would scarcely hold good at the present time, in view of recent developments in the methods of freezing and transport of fruit, and such developments should receive attention in any future revision of the regulations.

Sulphur dioxide must not be used for products which it is intended to pack in tinplate cans, as it has a marked effect on the corrosion of tinplate, and is liable to cause blackening (see p. 127). Fruit canners are therefore faced with the alternatives either of providing sufficient plant to cope with the fruit within a short time of its arrival at the factory or of making use of cold storage. Their choice will depend on economic and other special factors connected with their business.

(B) Methods of Manufacture of Jams and Jellies.

It is not intended in this work to give an account of the different types of plant or of the mechanical arrangements which may be used in a jam factory ; nor is it proposed to give a list of recipes for making jams and jellies. It is necessary, however, to give the broad outlines of the process so as to indicate how the underlying principles dealt with previously may best be applied.

Apart from the sorting and removal of leaves, stalks and undesirable portions of the fruit, which can only be done by hand, most fruit requires treatment of some kind before it enters the boiling-pan. Strawberries, for example, are washed and sometimes lightly crushed between wooden rollers ; raspberries are either heated in wooden vats, provided with steam nozzles, or steam-coils of non-corrodible metal, and passed through sieving-machines to remove the central cores (" plugs "), etc., or they may be passed through these machines in the raw state. Plums are heated in vats with a minimum of water until soft, when they may be sieved to remove stones for stoneless plum jam. Cherries are similarly treated. Currants are passed through machines which remove the stalks (this need not be done when they are intended for jelly) and are then heated in vats with a minimum of water. Gooseberries are whirled in machines lined with carborundum to rub off the " tops " and " tails," which are washed away in a stream of water. Oranges for marmalade are peeled by hand or machine and the peel cut by special machines into slices of any desired size or shape. These slices need to be softened * either by

* The addition of small quantities of carbonate of soda or ammonium hydroxide in softening peel is in no wise harmful to the consumer. The action of these alkalis probably consists in removing from the cell wall many substances which would otherwise toughen when boiled with sugar. Ammonia is less drastic in its action than soda and is, in many respects, preferable for use, since there is less danger of the peel breaking up into small fragments, which would appear unsightly. It may be that this is due to the fact that soda dissolves both hemicelluloses and pectoses, whereas the

prolonged boiling, or, more rapidly, by heating in water containing a small percentage of sodium carbonate or ammonia, or by heating with water in an autoclave under pressure (10-15 lb.), otherwise they become very hard and tough after being boiled with sugar. The centres are usually crushed between wooden rollers and then boiled with a measured quantity of water in wooden vats, the resulting pulp being passed through sieving machines to remove pips and hard portions. The pulp and peel may be united in the "boil" in the proportions in which they occur in the fruit or in other proportions, according to the type of marmalade required. If it is not desired to prepare the finished product at once, the pulp and peel should be brought together in the correct proportions, mixed and sterilised by heat in large bottles, which are hermetically sealed by means of metal caps, or the mixture may be stored in barrels with sulphur dioxide.

The preliminary treatment of fruits serves to liberate the natural pectin. Plums, gooseberries, currants and oranges usually contain enough of this substance to make a sufficiently stiff jam. Strawberries, raspberries and cherries, on the other hand, are deficient in pectin of good setting quality, and, unless the recipe contains a very high percentage of fruit—so high as to be unprofitable at normal prices—it is difficult or impossible to make a jam from them which is stiff enough to travel. It is therefore necessary in these cases to add an extract prepared from fresh fruits, such as apples or gooseberries, which are rich in pectin, and this has been the practice

former are said to be insoluble in ammonia; in any case it would appear that some research is required as to the precise causes of the softening.

The time required to soften peel in an autoclave depends on the size of the slices and on the pressure and temperature employed; some discoloration may occur if too high pressures are used.

With all these processes it is possible to make arrangements for collecting the oil of orange which would otherwise be lost, and, if soda or ammonia is used, the process can be made continuous. It would be possible to avoid handling the peel after it has been softened by carrying out the softening in perforated baskets of non-corrodible metal, each containing sufficient peel for one "boil" of marmalade.

of most jam manufacturers for many years. These extracts have, however, now been largely replaced by colourless and tasteless commercial preparations of pectin (p. 19) made from apple pomace or citrus peels and sold either as a concentrated liquid or in powdered form (see p. 20).

Standards for Jams.

The use of pectinous juices or commercial pectins has led to certain obvious abuses which may be almost impossible to detect by analysis, since it renders easy the manufacture of artificially coloured jams or jellies containing a relatively small amount of the fruit specified on the label. Such products may, to the casual observer, compare favourably in appearance with full-fruit products and so may compete seriously with them, thus lowering the general standard.

For this reason, certain standards for jam have now been agreed upon by the Food Manufacturers' Federation in collaboration with the Society of Public Analysts.* By this arrangement it is laid down that all jams (both first and second quality) shall contain not less than $68\frac{1}{2}$ per cent. of total soluble solids as shown, when cold, by the refractometer.

Standards have also been fixed for first and second quality jams on the basis of the quantity of fruit or fruits used in making 100 lb. of the finished product. These two grades are labelled "Full Fruit Standard" and "Lower Fruit Standard," respectively, and such an agreement, if loyally adhered to, should be satisfactory to manufacturers and consumers.

The standards fixed are as follows :—

PERCENTAGE OF SOLUBLE SOLIDS.

All jams, whether of first quality or second quality, shall contain not less than $68\frac{1}{2}$ per cent. total soluble solids, as indicated by the refractometer reading when cold, and not corrected for insoluble solids.

* *Analyst*, "Standards for Jams," 1930, **55**, 695.

FRUIT CONTENT FOR FIRST-QUALITY JAMS.

Single-Fruit Jams.

The minimum percentage of fruit content in finished jams of first quality (or, expressed in other terms, the number of pounds of fruit required to be used in making 100 lb. of finished jam) in each of the following named varieties shall be :—

	Fruit Content. Per Cent.		Fruit Content. Per Cent.
Strawberry . .	42	Red plum . .	40
Raspberry . .	38	Damson . .	38
Black currant . .	30	Apricot . .	40*
Red currant . .	35	Blackberry . .	38
Green gooseberry . .	35	Loganberry . .	38
Red gooseberry . .	40	Cherry . .	45
Greengage . .	40	Peach . .	40*
Victoria plum . .	40	Rhubarb . .	45
Green or golden plum	35		

Mixed Jams.

The minimum percentage of fruit content in mixed jams and the minimum proportions of each named fruit present shall be as follows :—

	Fruit Content. Per Cent.		Fruit Content. Per Cent.
Strawberry and gooseberry	40 (20/20)	Apple and plum . .	40 (30/10)
Gooseberry and strawberry	40 (30/10)	Blackberry and apple	40 (20/20)
Raspberry and gooseberry	40 (20/20)	Apple and blackberry	40 (30/10)
Gooseberry and raspberry	40 (30/10)	Household two-fruit	
Raspberry and red currant	40 (20/20)	jams, or any other	
Plum and apple . . .	40 (20/20)	jams not mentioned	
		in the schedule . .	40

For *two-fruit jams* the figures in brackets denote the respective proportions of each named fruit required to be present. The proportions for two-fruit jams not specially mentioned must be on the same basis.

* For apricot and peach jams, the equivalent of 4 five-kilo tins of apricot or peach pulp, containing no added water, must be present.

Fruit Juice and Pectin.

In the case of jams conforming to the standards for first quality, no declaration of added fruit juice and/or pectin shall be required.

FRUIT CONTENT FOR SECOND-QUALITY JAMS.

Single-Fruit Jams.

Single-fruit jams of second quality shall contain not less than 20 per cent. of the named fruit :—

	Minimum Fruit Content, Per Cent.		Minimum Fruit Content, Per Cent.
Strawberry . .	20	Red plum . .	20
Raspberry . .	20	Damson . .	20
Black currant . .	20	Apricot . .	20*
Red currant . .	20	Blackberry . .	20
Green gooseberry . .	20	Loganberry . .	20
Red gooseberry . .	20	Cherry . .	20
Greengage . .	20	Peach . .	20*
Victoria plum . .	20	Rhubarb . .	20
Green or golden plum	20		

Mixed Jams.

The minimum percentage of fruit content in mixed jams of second quality shall be 20 per cent., and the minimum proportions of each named fruit present shall be as in table on opposite page.

MARMALADE MADE FROM CITRUS FRUIT.

Citrus-fruit marmalade shall be made from citrus fruit only, and shall contain 68½ percentage of soluble solids.

* Apricot and peach jams, the equivalent of 2 five-kilo tins of apricot or peach pulp, containing no added water.

	Minimum Fruit Content, Total Proportion Per Cent.		Minimum Fruit Content, Total Proportion Per Cent.
Strawberry and gooseberry	20 (10/10)	Apple and plum	20 (15/5)
Gooseberry and strawberry	20 (15/5)	Blackberry and apple	20 (10/10)
Raspberry and gooseberry	20 (10/10)	Apple and blackberry	20 (15/5)
Gooseberry and raspberry	20 (15/5)	Household, two-fruit	
Raspberry and red currant	20 (10/10)	jams, or any other	
Plum and apple	20 (10/10)	jams not mentioned in the schedule	20

For *two-fruit jams* the figures in brackets denote the respective proportions of each named fruit required to be present. The proportions for two-fruit jams not specially mentioned must be on the same basis.

FRUIT JELLIES.

The percentage of the named fruit to be used in the manufacture of jellies shall be the same as that laid down for first quality and second quality jams of the same description, and the jellies shall be labelled similarly, except that the word "jelly" shall be substituted for "jam" in the warranty.

Acidity and Colour.

The use of citric, tartaric and malic acids is permissible, without declaration, for the purpose of acidifying jams, where the fruit used is deficient in acid. The use, when necessary, of permitted artificial colouring matter in jams is also allowed, without declaration.

The Basis of a Recipe.

On the basis of the specification just mentioned, and allowing for soluble solids such as acids and pectin, it will be seen that the finished jam or jelly, no matter what the grade, will contain approximately the quantity of sugar found necessary to give the maximum strength of the pectin-sugar-acid gel. It may be assumed that about 3 per cent. of the total weight of the jam

is represented by sugar derived from the fruit ; hence about 65 per cent. is added sugar. This figure will therefore form the basis of the recipe for jam or jelly, the quantity of fruit to be added depending on the agreed standards already mentioned, or on the nature of the product which the manufacturer wishes to produce. If the fruit which is being used is deficient in pectin or acid, or both, or if the quantity of fruit in the recipe is small, it will be necessary to add a proportion of these ingredients so that a gel of sufficient firmness and with a final p_H of approximately 2.45 (Ogg) may be obtained. With this end in view, the p_H value 3.1 found by Tarr to be most suitable for the fruit or fruit juice, and pectin, before the sugar is added, should be a guide, but it must be remembered that this figure relates to the conditions of a particular experiment. The figures obtained by research thus constitute a valuable theoretical basis for practice. It is necessary, however, to carry out trial "boils" in which the ingredients and the final products are carefully weighed and tested, and to make such adjustments as are necessary on the strength of these tests.

Jam Boiling.

In all jam or jelly boiling the immediate indicators of the end-point are a thermometer of special pattern (usually with a Fahrenheit scale), and a long-handled, flat spoon or "skimmer," made of silver, copper or aluminium. When the thermometer has risen to about 218°-220° F., the jam boiler begins to test for jellying properties by dipping the skimmer into the boiling mass and observing the manner in which the jam or jelly falls from the edge. At first it merely runs off in a stream, showing that the end-point has not been reached. Later, however, it begins to thicken, and finally it shows a tendency to gel by "flaking off" or breaking off clean. This usually occurs somewhere between 220° and 223° F., according to the barometric pressure and the nature of the product which is being boiled, and some experience is required in judging the exact moment for cutting off the steam and emptying the pan so as to obtain

the optimum gel. The whole process should not occupy more than ten minutes.

The practical tests already mentioned are supplemented by tests in the laboratory (see p. 71) in order to determine the total solids and the degree of inversion of the sugar ; it is also necessary to determine the weight of the finished " boil " so that the percentage of added sugar may be calculated. If the percentage of total soluble solids is found to be too high it will be necessary to add more pectin or acid or both ; if too low, i.e. if the jelly forms too soon, an excess of pectin is indicated, and a further trial boil must be made until all requirements are met. It is also advisable to see that 30-50 per cent. of the sugar is inverted, to avoid crystallisation of either cane sugar or glucose * on standing.

With experience, one or two trial boils will usually suffice, but the thermometer and " skimmer " should be used continually throughout the day's run, and the jam should be tested in the laboratory at frequent intervals in order that any variation in the materials, negligence on the part of the jam boiler, or other sources of trouble, may be detected and amended. The boiling is carried out in jacketed pans heated by steam under a pressure of 60-80 lb. These pans are usually made of copper, in which case it is good practice to have them heavily silvered inside ; nickel, monel metal, aluminium and stainless steel pans are also used.

The weight of a finished " boil " usually ranges from 100 to 120, or even 140 lb. It has already been pointed out that prolonged heating tends to destroy the setting power of the pectin, hence it is necessary to adjust the recipe and the steam pressure in accordance with this principle. The material is caused to boil as rapidly as possible, frothing being prevented by the addition of a little butter or other oil, and the water to be evaporated is cut down to a minimum. It is good practice,

* If the percentage of invert sugar is very low, cane sugar may crystallise out ; if very high, the jam may develop into a honey-like mass due to the formation of small crystals of glucose.

especially if the "boils" are large,* or if syrup † is used instead of sugar, to add the pectin in concentrated form.

Generally speaking, boiling need not be prolonged more than is necessary to cook and sterilise the fruit, to liberate the pectin (if this has not already been done), to ensure the thorough mixing and dissolution of the soluble ingredients, and to bring about the necessary degree of inversion of the sugar. The latter is a function of duration of boiling and acidity; if too low, it may be corrected by the addition of citric or tartaric acids (1 or 2 oz. per "boil" is usually sufficient) by the addition of a proportion of the sugar in the form of inverted syrup of known strength, or by prolonging the boiling period; if too high, the boiling period must be shortened by decreasing the quantity of water to be evaporated by using dry sugar and concentrated pectin, or, if this is already being done, by decreasing the size of the "boil." As soon as the boiling is complete, the steam is cut off from the pan and the jam or jelly is emptied by tilting into a water-cooled trough, where it is stirred gently until the solids (fruit, orange peel, etc.) no longer float. It is then filled into jars either mechanically or by hand, the surface is covered with a thin disc of waxed tissue paper, and the jam is allowed to cool. If the output is large, it will be necessary to cool the filled jars artificially in a cooling tunnel or chamber through which air is drawn by fans. When cool the jars pass into the stores, where they are stacked.

Alternative Methods of Boiling Jam.

(I) *The Vacuum-pan Method.*

This is practised to some extent, especially in America, where vacuum pans have been designed for this purpose. Such

* The modern tendency is to add pectin in concentrated form (3.5 per cent. solution), thus keeping the quantity of water to be evaporated low. In this case, the output from a boil may be from 130 to 150 lb.

† For reasons of cleanliness, e.g. when making light-coloured jams or clear jellies, it may often be preferable to use filtered syrup of known strength instead of dry sugar, the best of which may contain specks of insoluble matter which mar the appearance of the product.

pans are, however, necessarily more expensive than those of the open type, the process is somewhat more difficult to control, the output is less, and any improvement in the resulting product doubtful or, at any rate, difficult to detect.

(II) In the case of the lower-grade jams, which only contain about 20 per cent. of fruit, it is possible, by using concentrated pectin, to cut down to a minimum the quantity of water to be evaporated and, consequently, the time of boiling. This preserves to some extent the delicate, volatile flavours of the fruit, which tend to disappear after prolonged boiling. It is even possible to adjust the recipe so that $68\frac{1}{2}$ per cent. of sugar is present initially and no water need be removed. The jam can then be boiled in pans fitted with lids to which a reflux condenser is attached or heated in closed vessels of the autoclave type, fitted with stirrers. In the latter case, however, care must be taken that the temperature does not exceed the normal boiling-point. Also, attention must be paid to the inversion of the sugar, which must be adjusted, if necessary, as already described.

Storage.

Storage is one of the most serious problems which the jam manufacturer has to face, unless the modern method of capping the jars with metal caps as soon as they are filled is adopted. The surface of jam is a medium on which moulds and also mites will grow unless the stores are kept dry. On the other hand, if conditions are too dry, undue evaporation and consequent surface-graining and shrinkage may occur. Ideal conditions are therefore difficult to attain and control.

According to Tomkins,⁷ the humidity of the atmosphere has little effect on the growth of moulds when the conditions allow the moulds to draw their moisture freely from the substratum. With a substance like jam, however, where the quantity of available water is limited owing to the high concentration of sugar, and where movement of water from below upwards is

slow, especially if the surface is covered by a closely adherent waxed tissue, the humidity of the atmosphere is likely to have a considerable effect. Tomkins states that the growth of most fungi stops when they are *completely* exposed to a humidity as low as 90 per cent. The quantity of water available to a fungus on the surface of jam is not known, but experience shows that a store kept cool at an even temperature, and maintained at a humidity of about 80 per cent., is reasonably satisfactory.

Yeasts may gain a footing in jam which is too slack, but seem unable to penetrate if the gel is sufficiently firm.⁸ The author has seen yeasts growing freely in all kinds of jams which have been disturbed and artificially inoculated, even when the sugar concentration was as high as 72 per cent. The trouble from fermentation by yeasts, is, however, relatively slight when jam or jelly is properly made.

However good the storage conditions may be, it is always necessary to inspect and recondition the surface of jam, stored in open jars, by removing the old tissue and replacing it by a fresh one, which may have been treated with some preparation to inhibit the growth of fungi. This is advisable because moulds develop more readily in the closed space at the top of the jar, after wrapping, than under open conditions, and it is for this reason that the covers and outer wrappings should not be applied until the jam is about to be dispatched for sale.

Deterioration in storage is now largely prevented by hermetically sealing the jars, while still hot, in a sterile manner with metal caps fitted with rubber gaskets. Many patent caps of this kind have been devised which can be placed in position, sterilised by steam jets in a steam box, and finally held firmly through creating a partial vacuum in the headspace of the jars either by a specially constructed vacuum-machine or merely by screwing them up tightly while still hot. Jars sterilised and sealed in this way form an ideally hygienic package, and are to a very large extent independent of storage conditions.

Colour Changes During Storage.

See under "Discoloration in Fruit Products."

(C) Chemical Control of Jam Manufacture.

Jam or jelly-making is essentially a process which lends itself to control by the works' chemist.

The basis of methods for estimating the pectin in pectinous materials such as fruits, fruit juices or commercial pectins, has already been indicated. It is also quite simple to devise small-scale setting tests for these materials, by diluting if necessary, adding sugar, and boiling down to such a weight that there will be 68 per cent. of sugar in the finished jelly, which must be allowed to set under standard conditions.* A series of such tests, in which the acidity is varied, can be made to indicate what addition of acid may be necessary to obtain a gel of maximum strength. Such observations may be coupled with tests of the p_H -value of any pectinous solution to be used in jam-making by means of the quinhydrone,⁹ or, better still perhaps, the glass electrode.⁹

Raw material, such as sugar, should be examined by the polarimeter for sugar content,¹⁰ for cleanliness by inspecting the appearance of a solution of definite strength in water, and for ash. It is important that sugar used for jams and jellies should be free from both soluble and insoluble impurities.

Samples of finished jam or jelly should be taken at intervals during manufacture, and tested for content of total soluble solids and for inversion of sugar.

The total soluble solids are best measured by means of a refractometer of the Abbé or Zeiss type, specially graduated for sugar determinations. With jellies, a little of the sample may be placed on the prism of the refractometer and a direct reading obtained; with jams the sugar is not evenly distributed

* L. Geret (*Mitt. Lebensm. Hyg.*, 1930, 21, 116) has recently described a test in which 5 c.c. of alcohol is added to 15 c.c. of the juice to be tested in a narrow tube. The mixture is kept at 0° C. for one hour and then compared with standards.

between the liquid and solid portions: hence, for accurate results it is necessary to take a known weight of the sample (say 50 grams), add water, and boil gently for about five to ten minutes, cool, bring to a known weight with water (say three times the original weight of the jam), stir well, filter, determine the content of total soluble solids in the solution by refractometer (or by specific gravity determination),* and calculate the percentage in the original jam. Some materials, such as marmalade containing a large proportion of the fruit tissue, should be well mixed and minced in a machine and pounded in a mortar with water while being brought into solution.

For rapid testing, a value for the total solids in the liquid portion of the jam may be obtained by squeezing some of the syrup from the sample on to the prism of the refractometer through cambric or muslin, and reading off the total solids. A correction based upon a more accurate method may then be applied. This correction depends upon factors such as the quantity and character of the insoluble solids in the jam, and the duration of boiling, hence it differs according to the kind of fruit and must be revised if the recipe is altered.

The degree of inversion of the sugar is best tested by the method of Lane and Eynon,¹¹ in which the end-point in the reduction of Fehling's solution is detected by the use of methylene blue as an indicator. Fifteen grams of the jam or jelly, in which the total soluble solids have already been determined by the refractometer, are dissolved in *cold* water, and the volume made up to a litre. The solution, which contains approximately 1 per cent. of sugar, is strained through calico and titrated against 10 c.c. of Fehling's solution maintained at boiling temperature. When the solution is almost decolorised, two or three drops of methylene blue are added, and the titration continued until the liquid is again colourless. From this titration the quantity of invert sugar present in the solution can be

*This gives slightly more accurate results than the refractometer, as the errors due to soluble solids other than sugars are less (see Table XII.; also Table XIV. for sp. gr. of sugar solution).

calculated.* Also, if the percentage of soluble solids found in the jam by the refractometer be regarded as sugar, the percentage of inverted sugar can be calculated with sufficient accuracy for works' purposes.

The limits for the percentages of total solids and invert sugar which should be found in jam have already been indicated (p. 67), and any samples which fall outside these limits should be at once reported, so that the necessary adjustment (p. 68) may be made.

The acidity of jam is determined by taking 10 grams of the sample, dissolving in water, and titrating, while boiling, with $\frac{N}{10}$ caustic soda, using phenolphthaleïn as indicator.

If difficulty is experienced in observing the end-point, it may be convenient to use phenolphthaleïn paper as an external indicator and to work at a considerable dilution. Electro-metric methods may also be used (see also p. 134).

TABLE XII. (after Macara).

Substance.	Percentage in Sample.	Correction.	
		Refractometer.	Specific Gravity at 20° C.
Invert sugar .	20	+ 0.45	— 0.07
	40	+ 0.90	— 0.14
	60	+ 1.35	— 0.21
Glucose solids	20	— 0.25	— 0.34
	40	— 0.5	— 0.68
Citric acid .	1	+ 0.1	— 0.09
	2	+ 0.2	— 0.18
	3	+ 0.3	— 0.27

* Ten c.c. of Fehling's solution is equivalent to 0.05 gram of invert sugar, which is derived from 0.0475 gram of cane sugar. Hence the result may be stated either as the percentage of invert sugar in the jam or as the percentage of the sugar which has become inverted. A formula for the calculation of this is $\frac{31666.7}{nx}$ where n = number of c.c. jam solution required for 10 c.c. of Fehling's, and x = the percentage of soluble solids in the jam.

The foregoing tests are, as stated, merely intended for rapid works control. For more accurate determinations Macara ¹² gives in Table XII. the corrections to be applied for invert sugar, glucose solids and citric acid, when using the refractometer to estimate the total soluble solids. A correction is also applied for the effect of the insoluble solids.

For the application of the above table, Macara gives the following example.

Example I.—A sample of black currant jam gave the following results on analysis :—

Insoluble solids	2.0 per cent.
Invert sugar	31.0 „
Acidity as citric acid . . .	0.95 „
Direct refractometer reading	n_D^{20} 1.4673

Now n_D^{20} 1.4673 corresponds with 70.9 per cent. of soluble solids as sucrose.

Correction for invert sugar	+ 0.7
„ „ acid	+ 0.1
Total	71.7

This is corrected for insoluble substances thus :—

$$\frac{71.7 \times (100 - 2.0)}{100} = 70.3 \text{ per cent.}$$

For determination of soluble solids by the specific gravity method, Macara makes up a 20 per cent. solution of the jam by dissolving 50 or 100 grams of the jam in water at a low temperature and filtering through muslin or a fine sieve. The gravity is determined by the usual methods at 20° C., and the percentage of solids in solution calculated as sucrose, using the factor 3.845. From this the solids in the original sample are calculated and corrections applied for invert sugar, etc., as in the Table.

Example II.—Black currant jam as in I.

Specific gravity of a 20 per cent. solution = 1.05423.

Soluble solids as sucrose, $\frac{54.23}{3.845} \times \frac{100}{20} = 70.5$ per cent.

Correction for invert sugar . . . = — 0.1 „

„ „ acid . . . = — 0.1 „

Total sugar = 70.3 „

The correction for insoluble solids in this case is :—

$$\frac{70.3 \times (100 - 0.4)}{100} = 70.0.$$

Macara states that the discrepancy between the two methods (0.3 per cent.) is larger for black currant than for most jams on account of the salts and colours present. For jams like strawberry and apple the results often agree within 0.1 per cent. In a case like the above, the mean of the two methods is taken.

REFERENCES.

JAMS AND FRUIT JELLIES.

- 1 MORRIS, T. N., and BRYAN, J. M., "Cold Storage," F.I.B. Ann. Report, 1929, p. 95.
- 2 MORRIS, T. N., *ibid.*, 1930, p. 127.
- 3 MORRIS, T. N., and BARKER, J., "The Preservation of Fruits and Vegetables in the Frozen State," *ibid.*, 1931, p. 129.
- 4 JOSLYN, M. A., "Preservation of Fruits and Vegetables by Freezing Storage," Univ. Cal. Agric. Exp. Sta., Circular 320, 1930.
- 5 BARKER, B. T. P., and GROVE, O., "Sulphur Dioxide as a Preservative for Fruit," *J. Pomology and Hort. Sci.*, 1925, 5, 50.
- ANONYMOUS, "Standards for Jams," *Analyst*, 1930, 55, 695.
- 6 WILLIAMS, J., and CORRAN, J. W., "The Preservation of the Antiscorbutic Vitamin in Lemon Juice," *Biochem. Journ.*, 1930, 24, 37.
- 7 TOMKINS, R. G., "Studies of the Growth of Moulds," *Proc. Roy. Soc.*, 1929, 105B, 375.
- 8 HIRST, F., "The Effect of Sugar, Acid, and 'Set' on the Keeping Properties of Jams," Univ. Bristol Ann. Report of the Agric. and Hort. Res. Sta., Long Ashton, Bristol, 1927, p. 150.
- 9 CLARK, W. M., "The Determination of Hydrogen Ions," The Williams and Wilkins Co., Baltimore.

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- 10 BROWN, C. A., "Handbook of Sugar Analysis," New York, 1912.
- 11 LANE, J. H., and EYNON, L., "Determination of Reducing Sugars by means of Fehling's Solution with Methylene Blue as Internal Indicator," *J. Soc. Chem. Ind.*, 1923, 42, 321.
- "Preparation of Fehling's Solution for the Volumetric Determination of Reducing Sugars," *ibid.*, 1925, 44, 150.
- 12 MACARA, T., *Analyst*, 1931, 55, 353.

PART II.
THE CANNING OF FRUIT.

CHAPTER IV.

GENERAL ACCOUNT OF THE PROCESSES.

THE principle of sealing foodstuffs hermetically in containers and sterilising them by heat so that they can be stored indefinitely was invented in 1804 by a Frenchman, Nicholas Appert, who was awarded a prize for the process, and established a business house which still exists for carrying out canning operations on a commercial scale. It is not proposed to describe the mechanical details or the machinery used in canning any more than was done in the case of jam-making, although both industries lend themselves to highly specialised mechanisation. In subjects such as the composition of fruits, the fruit colours, storage of fruits, time of picking and choice of varieties, there is much that applies to both canning and jam-making, although there are certain differences as regards storage which have already been mentioned (p. 59). For instance, it must be made quite clear that sulphur dioxide must not be used for preserving fruit intended for canning. If the fruit is not used fresh it must either be preserved temporarily at temperatures between 32° and 40° F. or covered with syrup of canning strength and frozen and stored at 14° F. or under (see p. 55).

Colour, flavour and texture are the important considerations in choosing the time for picking and the particular variety of fruit to be canned. Hirst and Adam¹ give an account of canning trials with a great many varieties of English fruits, and their work should be studied by those anxious to pursue this subject. These writers find that strawberries, which tend to turn brown in canning, require the addition of an artificial

colour, the best obtainable for this purpose being Ponceau 2 R. It was found that variations in the final colour of the product were due to differences in the stability of the natural fruit colour rather than to a difference in the capacity of berries of different varieties to absorb the artificial colour evenly. The flavour of the canned product depended largely on the ripeness of the fruit at the time of canning, and the flavour of strawberries was often affected by the length of time which had elapsed between picking and canning. The use of sulphur sprays as fungicides may also give canned strawberries an extremely disagreeable flavour, hence canners are advised to ascertain whether such sprays have been used. Other things being equal, the varieties of soft fruits which are best from the canner's point of view are those of firm texture which withstand handling and transport with the minimum amount of damage.

Fruit for canning should have attained its maximum size and have its colour fully developed (except in the case of gooseberries, which are canned green), but must not be too ripe. Under-ripe fruit will shrivel or toughen when canned, and may fail to recover its shape; over-ripe fruit, on the other hand, will break down and appear unsightly. These changes in texture are doubtless connected with the composition of the cell walls, and especially with the condition of the pectic substances. The skins of fruit (e.g. plums), should preferably remain unbroken, and the flesh firm after cooking. Thus, on the whole, greater care is required in choosing varieties and having the fruit of uniform ripeness for canning than for jam-making.

The sequence of processes in canning is as follows :—

1. Sorting, grading and washing the fruit; removal of stalks, calyces, etc.
2. Preparation of the sorted fruit for canning (peeling, coring, trimming, steam blanching).
3. Filling into cans.
4. Syruping.

5. Exhausting.
6. Lidding and sealing cans.
7. Processing or sterilisation by heat.
8. Cooling.
9. Storing (spoilage and corrosion).

Fruit Sorting, Grading, etc.

It is obvious that these are mainly mechanical operations carried out in the interests of hygiene and in order to give an attractive appearance to the finished product. It may be pointed out here, however, that there is a good deal of evidence that over-ripe and stale fruit, besides being unsightly and of poor flavour, causes more trouble from perforations and hydrogen swells than fruit in prime condition. This has been noticed repeatedly in commercial canning and in experiments with fruits stored for different lengths of time. It is, possibly, connected with the fact that such fruit loses acidity (see p. 4) and is also richer in substances, formed either by the activity of oxidases or by direct oxidation, which accelerate corrosion in the can by providing the oxygen necessary for detinning (see under "Spoilage"). Stale fruit is also more heavily charged with micro-organisms than fresh fruit, and this, coupled with a decrease in acidity, lengthens the time required for sterilisation. From all these points of view, therefore, sorting must be carried out carefully, so as to exclude stale, over-ripe, or damaged fruit.

Grading is merely a question of pleasing consumers and suiting the size of fruit to the size of can used. Very small fruit is unsuitable for canning, although quite good for jam ; it is good practice, however, to fill large cans with large fruit and smaller cans with moderate-sized fruit. Grading also has a relation to questions of filling and standardisation in so far as it affects the proportion of fruit to syrup, since it may be found to be impossible to fill the correct weight of large fruit of awkward shape into small cans (see p. 87, "Filling").

Preparation of Fruit for Canning.

Many fruits require no treatment beyond the removal of stalks, calyces, etc., and washing, where possible, before filling into cans ; it is obvious, however, that some delicate fruits, like raspberries, cannot be washed without injury. Apples, pears, pine-apples and mangoes must be peeled, cored or pitted, as the case may be, and sliced ; peaches are peeled with the help of soda-lye (lye-peeling), and afterwards sliced and pitted. Tomatoes are blanched either in hot water or steam to cause the skins to come away easily ; if required for *purée* or paste they may be passed through a cyclone (sieving-machine), to remove skin and pips. Apricots are cut in halves and stoned ; cherries may also be " pitted." Grape-fruit must have the outer rinds and " whites " removed, and each segment must also be skinned separately. Gooseberries are graded and then treated as for jam (see p. 60) ; and there is no doubt that the removal or perforation of the epidermal tissues caused by this process facilitates the attainment of pressure-equilibrium between syrup and fruit juice, thus lessening the tendency to shrivel.

Some of these processes, like the lye-peeling of peaches and the treatment of apples and tomatoes, deserve special mention, as they require some skill and have been the subject of special research.

Scalding and Lye-peeling.

In the early days of canning, fruits were peeled by hand with a knife. Since that time machinery has been developed to replace much of the hand-labour. Success has also been attained in softening the skin of certain fruits by scalding them in hot water or steam, or by the use of caustic soda or " lye," so that it may be removed easily by rinsing or with a brush.* Tomatoes are peeled by scalding them for a short period and

* Care must be taken that soaking in lye is not too prolonged, and that the solution is kept at the right strength (see also under " Drying," p 179).

then dropping them into cold water, when the skin is readily removed by hand or machine ; certain varieties of freestone peaches are easy to peel by hand, after they have been split in half and passed through a steam-box. Bitting² studied the peeling of certain varieties of peaches and other fruits, such as pears and quinces, by means of soda-lye. These experiments were carried out in a tank divided into three compartments through which the fruit was passed. This was arranged so that lye of varying strength might be used in one or two, or in all three compartments, or so that water might be substituted for lye in any particular compartment. It was found most effective to have hot water in the first compartment, hot caustic soda of 3 per cent. strength in the second, and hot caustic soda of 1.3 per cent. strength in the third. The period of immersion in each bath was twenty seconds, and the strength of the third bath was maintained by overflow from the second, the object of this bath being to prolong the action on green portions and spots. The fruit then passed into a washer in which the loosened skin was removed either by the action of sprays or sprays and brushes combined. A later type of washer was also mentioned, which consisted of a tank having compartments filled with water. Simple lifting of the peaches from one compartment and dropping them into the next was found to effect complete removal of the skin. Lye has also been used with success in peeling vegetables like carrots, sweet potatoes and maize.

Pre-cooking or Steam-blanching.

It is often advantageous to blanch fruits and vegetables either with steam or hot water, so as to soften and shrink them in order to obtain a well-filled can or bottle after cooking. This process has the further advantage of driving out from the tissues a great deal of air which might otherwise remain to promote corrosion (see under "Spoilage"). Apple slices notably require steaming if a solid pack is to be obtained. The

slices are steamed until they begin to soften, but care must be taken that they do not disintegrate. The duration of steaming depends a good deal on the variety and condition of the apples, and some experience and judgment is required for success in this process. The slices should be given no opportunity to cool down after the steaming, but should be filled into cans as quickly as possible, covered with hot syrup or water, sealed and processed.

Kohman³ conducted a number of experiments with apples, and showed that the oxygen in the tissues was responsible for the production of hydrogen-swells and perforations, and was difficult to remove by the ordinary exhaust methods. He succeeded in overcoming this trouble by the prolonged soaking of the slices in a weak (2 per cent.) brine, which permitted an almost complete removal of oxygen through the respiration of the still-living tissue. Soaking, either in brine or in a dilute (5 per cent.) solution of cane sugar prevents apple slices from turning brown; even dropping them in cold water slows down this process. Prolonged soaking in brine also offers some advantage during subsequent steaming since it reduces the tendency for slices to break down. It has a serious disadvantage, however, in that it may sometimes cause a loss of flavour and result in a rather insipid and salt-tasting pack.

Some studies have been made by the author on the amount of air which could be collected from apple slices treated in various ways. The apples used in these tests were Bramley's Seedlings, a little too ripe for successful canning, and containing, perhaps, more than the normal amount of air. They serve, however, to illustrate the subject.

Fresh slices weighing 500 grams were placed in a large flask, which was then completely filled as quickly as possible with boiling water. The flask was placed in a bath of boiling water, a delivery tube, leading to a measuring cylinder, quickly inserted and the displaced air measured over different periods of time. After five minutes 68 c.c. of air were collected, after ten minutes 78 c.c., and after fifteen minutes 80 c.c. This gas contained

15.6 per cent. of carbon dioxide, 12.6 per cent. of oxygen, and 71.8 per cent. of nitrogen.

After being soaked in 2 per cent. brine for twenty-four hours, 500 grams of similar slices yielded 80 c.c. of gas containing 18 per cent. of carbon dioxide, 2.7 per cent. of oxygen, and 79.3 per cent. of nitrogen.

The quantity of air remaining in similar slices (unsoaked) after having been steamed for various lengths of time was also estimated as follows :—

Duration of Steaming. Minutes.	Air Collected from Steamed c.c. Slices.
1½	35
3	12.75 containing : CO ₂ 1.2 c.c. O ₂ 1.5 „ N ₂ 10.0 „
5	6.0

These tests, although somewhat crude, show that the brine-soaking undoubtedly has the effect of replacing most of the oxygen by carbon dioxide. At the same time, however, with apples steamed carefully for three to five minutes or sufficiently to soften them without breaking them up, the quantity of oxygen remaining in the tissues is also very small.

Kohman has shown that cooking unsoaked apples causes a considerable destruction of vitamin C, and he recommends prolonged brine soaking as a general practice for apples. The work of Zilva, however (p. 226), indicates that further research on this subject may be necessary.

Other methods involving the removal of oxygen, either under vacuum or in an atmosphere of an inert gas like nitrogen, are available if it is desired to avoid some corrosion and the loss of some vitamin C with apples canned without prolonged soaking. The author has, however, seen very good results, from the point of view of flavour and appearance, obtained merely by steaming fresh slices and having a brine tank between slicer and steamer to prevent undue browning during stoppages. There is evidence that this method by no means completely destroys the anti-scurvy value of apples which are rich in vitamin C.

Special Products.

Certain fruits, such as tomatoes,* ^{4, 5, 6} and sometimes strawberries and raspberries, are canned after conversion into a *purée* by means of a "cyclone" or sieving machine, which removes skin, and, if necessary, pips. For this purpose the fruit is first rendered soft by steaming or cooking for a short time and passed through the machine while hot. In the case of tomatoes the resulting *purée* is concentrated to a definite specific gravity in large vacuum pans, lined with glass or some non-corroding metal, filled into cans and processed. This *purée* may be mixed with vinegar, salt, sugar, various spices and flavouring materials and sometimes a little pectin, processed in bottles, and sold as Tomato Catsup. It may also be used as a basis for Tomato Soup.

Filling and Syruping: Standardisation of Canned Fruits.⁷

Filling and syruping may conveniently be considered together. Many products do not lend themselves to mechanical filling, hence this operation is often carried out by hand. Syruping, on the other hand, in large-scale canning is always accomplished by means of special machines which fill each can to a definite height with hot syrup.

The amount of headspace to be allowed is an important consideration, since over-filling may give rise during hot weather to swells or springers, or even to leaky cans through the severe strains on the seams due to the expansion of the liquid contents during processing. Moreover, with a very small headspace, there is little room for any hydrogen which may be produced through corrosion, so that hydrogen swells

* "Canned Tomatoes and Tomato Products," Bull. 97A, Nat. Cannery Assoc., Washington, D.C.

Bigelow and Stevenson, "Tomato Products," Bull. 21L, Nat. Cannery Assoc., Washington, D.C.

Bitting, A. W., "Methods Followed in the Commercial Canning of Foods," U.S.A. Dept. of Agric. Bull. 196.

will form more quickly than when a larger headspace is allowed. If the cans are "syruped" hot, as in modern practice, it is generally considered that filling to within $\frac{1}{4}$ to $\frac{5}{16}$ inch from the top of the can before the lid is rolled on is satisfactory. This gives a final headspace of about $\frac{1}{8}$ to $\frac{3}{16}$ inch, since the counter-sink of the lid should occupy $\frac{1}{8}$ inch.

The standardisation of canned fruits is also involved here. Standardisation is desirable from many points of view, especially from that of the consumers', who are entitled to know what to expect when they buy a can of a certain brand or grade. Apart from the quality and condition of the fruit, the main factors in standardisation are the weight of fruit and the quantity and strength of the syrup. An examination of the filling weights of a large number of cans has shown that a good average figure for soft fruits, such as raspberries and strawberries, is 0.61 * oz. (avoirdupois) of fruit per fluid ounce of filling space. For stone fruits the average is slightly higher, viz. 0.65 oz. per fluid ounce. The correct weight of fruit per can in ounces (avoirdupois) may therefore be determined by measuring the capacity of the can up to the filling line in fluid ounces, and multiplying the figure obtained by 0.61 for soft fruit and 0.65 for stone fruit. It is impracticable to weigh the fruit into the cans, but with experience and good supervision it is possible to fill to a given weight with considerable accuracy. The ripeness of the fruit may have to be taken into account; also wet fruit usually packs closer than dry fruit, and may cause over-filling.

The strength of the syrup should be tested by means of a hydrometer of the Baumé, Brix or any other type to which the operators may have become accustomed. Probably the Brix type is most convenient, because the figures on the scale represent sugar percentages.

Table XIV. shows the percentage of sugar by weight in

* This figure should not be exceeded even with fruits like red currants, which pack closely together. If a can is completely filled with currants the concentration of sugar will be too low unless a very strong syrup is used.

a syrup (degrees Brix), the corresponding readings on the Baumé scale at 60° F., the Baumé readings at boiling-point for the same strength of syrup, the corresponding readings on Twaddell's hydrometer at 60° F., the quantity of water per gallon of syrup in fluid ounces, the specific gravity and the weight of sugar per gallon of syrup.

Hydrometers in use for hot syrup should be made of glass rather than metal, should possess a good open scale, and should be tested occasionally to make sure that the scale has not slipped. Metal hydrometers are liable to corrode, and may become dented, or even perforated, in use, and so cause errors.

In order to calculate approximately the initial strength of the syrup which must be added in canning a given fruit so as to obtain a desired final strength, the following formulæ may be used :—

$$W_1 + W_2 = W_3, \quad . \quad . \quad . \quad (1)$$

$$W_1x + W_2y = W_3z, \quad . \quad . \quad . \quad (2)$$

where W_1 = the weight of fruit in the can,

x = the percentage of soluble solids in the fruit (see below),

W_2 = weight of added syrup per can,

y = percentage of sugar in the syrup,

W_3 = total weight of syrup and fruit in the can,

z = percentage of soluble solids in the final product.

The same formula also applies in a more general way if

W_1 = the weight of fruit per unit volume of the final product,

W_2 = the weight of syrup per unit volume of the final product,

and W_3 = the weight of a unit volume of the final syrup, i.e. the specific gravity of the final syrup.

The value of x must not be taken as the percentage of soluble solids in the raw juice, but as the soluble solids in the fruit

juice after cooking. It also includes any effect on the final result due to the insoluble solids, and must be determined as an average of a large number of tests in which it is the only unknown quantity. This value is given for a number of fruits in Table XIII.

The method of applying the formula to any specific case is as follows: Let us suppose that the final or "cut out" syrup strength required for canned strawberries is 30 per cent. of total solids. Then, taking the equation in its general form,

$$W_1 = 0.61 \text{ oz.},$$

$$W_3 = 1.13 \text{ oz. (from the specific gravity table, p. 92),}$$

$$W_2 = 1.13 - 0.61 = 0.52 \text{ oz.}$$

The value of x for strawberries from Table XIII. is 6.5. Substituting these values in equation (2) we have

$$0.61 \times 6.5 + 0.52y = 1.13 \times 30,$$

$$0.52y = 29.94,$$

$$y = 57 \text{ per cent.}$$

Having arrived at this value, further slight adjustments of the strength of syrup to be added should be made after actual trial, since the fruit which is being canned may differ slightly from the average.*

Some tests conducted by the author with raspberries at the Low Temperature Research Station, Cambridge, have some interest from the point of view of standardisation. These were intended to illustrate:—

- (a) the effect of varying the quantity of fruit in the can, keeping the syrup strength and filling-line constant;
- (b) the effect of varying the syrup strength with the weight of fruit and the filling-line constant;
- (c) the effect of wet and dry fruit on the filling.

* For instance, the raspberries used in the following tests had the value 13.7 for x , which is well above the average figure given in Table XIII. This was probably due to an exceptionally dry season.

Tall cans of 1 lb. capacity were used in all the experiments, and $\frac{1}{4}$ -inch headspace was given. The cans were turned once a day for ten days so as to mix the contents thoroughly and the results under the different heads are shown below :—

- (a) A variation of 1 oz. in the weight of the fruit caused a difference of 4 per cent. in the final syrup strength, for this size of can, when the syrup added contained 55 per cent. of sugar. The proportion 0.61 oz. of fruit per fluid ounce of filling space was satisfactory as regards the appearance and flavour of the contents when turned out.
- (b) A variation of 10 per cent. in the strength of syrup added caused a difference of 5.6 per cent. in the final syrup strength. A final product with a very low sugar-content was less bright in appearance than those containing a higher percentage of sugar. For raspberries it was thought that 32-33 per cent. of soluble solids in the final syrup as determined by the refractometer was most satisfactory as regards flavour.
- (c) As previously stated, wet fruit packs more closely than dry fruit. A 1 lb. tall can filled with wet fruit was found to contain 1 oz. more than a similar can packed with dry fruit, and on an average the strength of the final syrup was 2 per cent. less with wet fruit, a difference which could be detected by tasting.

From these tests it would appear that the quantities of fruit and sugar used in canning should be carefully controlled, both from the point of view of flavour and economy. An excess of sugar, to the extent of a few degrees Brix, does not necessarily improve the pack, but on the other hand, it may make it too sweet and entail a considerable loss to the canner on a season's run. The hydrometer should be in constant use, the final strength of the syrup in the cans should be carefully checked by hydrometer or refractometer, and small details, such as the

evaporation from hot syrup during delays and stoppages, should be watched and allowed for, if necessary.

TABLE XIII.

VALUES FOR x WITH VARIOUS FRUITS.

Loganberries	10.6
Blackberries	13.0
Raspberries	8.1 (see footnote, p. 89).
Strawberries	6.5
Red currants	14.0
Black currants	15.0
Morello cherries	12.6
Red cherries	10.0
White cherries	10.0
Victoria plums	10.0
Greengages	12.1
Damsons	11.6
Golden plums	9.4

Syrup Tables for Canning.

The strength of syrup to be used in canning different fruits will depend to a great extent on the individual taste of the canner and on the purpose for which the product is intended, but certain standards have been fixed under the British National mark scheme which meet with general approval in Great Britain. These are obtainable by application from the Ministry of Agriculture, but, for the most part, fall within the limits set in Table XV.

TABLE XIV.

SYRUP TABLE.

Table Showing Approximately the Quantity of Sugar and Water required for Syrups of Different Densities.

Per Cent. Sugar or Degree Brix.	Degree Baumé at 60° F.	Degree Baumé Boiling.	Degree Twad- dell at 60° F.	Specific Gravity at 60° F.	Water per Gallon of Syrup. Ozs.	Weight of Sugar (lb.) per Gallon of Syrup at 60° F.	Weight of Sugar (lb.) per Gallon of Water at 60° F.
12.5	7.1	4.2	10	1.050	147	1.31	1.4
13.5	7.7	4.8	11	1.055	145.25	1.44	1.55
15.0	8.3	5.4	12	1.060	144	1.59	1.76
16.0	8.9	5.98	13	1.065	143	1.79	1.9
17.0	9.4	6.48	14	1.070	142	1.81	2.03
18.0	10.0	7.07	15	1.075	141	1.94	2.2
19.5	10.5	7.66	16	1.080	139.5	2.06	2.4
20.5	11.2	8.26	17	1.085	138.25	2.20	2.5
21.5	11.8	8.85	18	1.090	137	2.31	2.7
22.5	12.6	9.75	19	1.095	135.5	2.47	2.9
24.0	13.2	10.25	20	1.100	134.25	2.60	3.2
25.0	13.8	10.84	21	1.105	132.5	2.75	3.4
26.0	14.4	11.44	22	1.110	131	2.90	3.6
27.0	14.9	11.94	23	1.115	130	3.04	3.8
28.0	15.4	12.43	24	1.120	128.75	3.17	4.0
29.0	16.0	13.03	25	1.125	127	3.31	4.2
30.0	16.5	13.45	26	1.130	125.5	3.43	4.4
31.0	17.1	14.05	27	1.135	124.25	3.69	4.6
32.0	17.6	14.55	28	1.140	123	3.71	4.8
33.0	18.2	15.14	29	1.145	121.5	3.86	5.0
34.0	18.6	15.54	30	1.150	120	3.95	5.3
35.0	19.2	16.14	31	1.155	119	4.06	5.4
36.0	19.8	16.74	32	1.160	118	4.20	5.7
37.0	20.3	17.10	33	1.165	117	4.34	5.9
38.0	20.8	17.65	34	1.170	115.5	4.48	6.2
39.0	21.4	18.25	35	1.175	114	4.62	6.5
40.0	21.9	18.75	36	1.180	112.5	4.76	6.8
41.0	22.4	19.25	37	1.185	111	4.90	7.0
42.0	23.0	19.84	38	1.190	110	5.06	7.3
43.0	23.5	20.33	39	1.195	108.75	5.15	7.6
44.0	24.0	20.82	40	1.200	107.75	5.25	7.9
45.0	24.6	21.41	41	1.205	106.75	5.37	8.2
46.0	25.1	21.90	42	1.210	105.5	5.5	8.5
47.0	25.5	22.29	43	1.215	104	5.6	8.8
48.0	26.1	22.88	44	1.220	103	5.78	9.2
49.0	26.6	23.37	45	1.225	101.75	5.89	9.5
49.5	27.2	23.96	46	1.230	100.75	6.0	9.7

TABLE XIV (*continued*).

Per Cent. Sugar or Degree Brix.	Degree Baumé at 60° F.	Degree Baumé Boiling.	Degree Twad- dell at 60° F.	Specific Gravity at 60° F.	Water per Gallon of Syrup. Ozs.	Weight of Sugar (lb.) per Gallon of Syrup at 60° F.	Weight of Sugar (lb.) per Gallon of Water at 60° F.
50.5	27.6	24.40	47	1.235	99.5	6.125	9.8
51.5	28.1	24.80	48	1.240	98.25	6.25	10.5
52.5	28.8	25.50	49	1.245	97.25	6.37	10.8
53.0	29.0	25.70	50	1.250	96	6.5	11.1
54.0	29.3	25.9	51	1.255	94.75	6.75	11.6
55.0	29.8	26.3	52	1.260	93.5	6.89	12.1
56.0	30.3	26.8	53	1.265	92.25	7.06	12.6
57.0	30.7	27.2	54	1.270	91.00	7.17	13.0
57.5	31.2	27.7	55	1.275	89.5	7.33	13.5
58.5	31.8	28.2	56	1.280	88.0	7.49	14.2
59.0	32.2	28.6	57	1.285	86.0	7.64	14.5
60.0	32.5	28.9	58	1.290	84.25	7.8	15.3
61.0	32.8	29.2	59	1.295	81.5	7.92	15.7
62.0	33.3	29.7	60	1.300	80.5	8.17	16.9
62.5	33.8	30.2	61	1.305	78.0	8.33	17.6
63.5	34.3	30.64	62	1.310	76.5	8.49	18.4
64.0	34.5	30.83	63	1.315	75.0	8.59	18.8
65.0	34.9	31.00	64	1.320	73.5	8.75	19.8
66.0	35.3	31.3	65	1.325	72	8.89	20.4
67.0	35.9	31.8	66	1.330	70.5	9.06	
67.5	36.3	32.1	67	1.335	69	9.17	
68.5	36.7	32.4	68	1.340	67.75	9.30	
69.0	36.9	32.5	69	1.345	66.25	9.48	
70.0	37.4	33.0	70	1.350	64.75		
71.1	38.0	34.0		1.357			
72.1	38.5	34.4		1.363			
73.2	39.0	34.9		1.370			
74.1	39.5	35.4		1.376			
75.2	40.0	35.9		1.383			
76.3	40.5	36.3		1.390			
77.3	41.0	36.8		1.397			
78.2	41.5	37.3		1.403			
79.3	42.0	37.8		1.410			
80.3	42.5	38.2		1.417			
81.4	43.0	38.7		1.424			
82.4	43.5	39.2		1.431			
83.5	44.0	39.7		1.438			

Absolute accuracy is not claimed for these figures, but they are near enough for practical purposes.

Figures given by Hirst and Adam ¹ for British fruits are as follows :—

TABLE XV.

Fruit.	Lb. of Sugar per Gallon of Water.	Degrees Brix at 68° F.	Degrees Baumé at 68° F.
Gooseberries .	6 to 8	38 to 44·4	20·6 to 24·5
Raspberries .	8 „ 10	44·4 „ 50	24·5 „ 27·3
Loganberries .	8 „ 12	44·4 „ 55	24·5 „ 29·5
Strawberries .	8 „ 10	44·4 „ 50	24·5 „ 27·3
Blackberries .	6 „ 8	38 „ 44·4	20·6 „ 24·5
Plums and Damsons .	6 „ 8	38 „ 44	20·6 „ 24·5
Black currants .	8 „ 10	44·4 „ 50	24·5 „ 27·3
Pears .	6 „ 8	38·4 „ 44	20·6 „ 24·5
Apples * .	water	—	—

* Apples in solid pack are considerably improved in appearance and flavour by the addition of a 50 per cent. syrup instead of water.

Exhausting, or the Removal of Air from the Can and its Contents.

This is usually accomplished in a large, covered tank containing hot water. The open cans, filled with fruit and “syruped” as hot as possible, are immersed in this to within about an inch of their tops, and travel through at a regulated rate. The water in the bath is kept at about 180°-190° F., and cans usually emerge with their contents at a temperature of about 160° F. The lids are then placed in position automatically, clinched on, and rolled tight by the double-seaming machine.

The following test shows that, at first, the syrup loses heat to the fruit more rapidly than it is absorbed from the bath, so that for a minute or two the temperature of the syrup actually falls. To illustrate this, fruit packed in 1 lb. cans was covered with syrup at 200° F., and passed through an exhaust tank which, in this case, was at a temperature of 205° F. In the first one-and-a-half minutes the temperature of the syrup fell to about 145° F., after six minutes it was 163° F., and took eight minutes to reach 170° F.

The importance of removing air from the tissues of the

fruit has already been mentioned (see p. 84). It is also important that, when the can is sealed, the air in the headspace should be replaced very largely by steam, so that, when the can is cool, there will be as high a vacuum inside as it will support without collapsing. With products which contain no air in the tissues it is possible to cover with the hot syrup and seal without passing through the exhaust tank and before the fall in temperature has time to occur. By this means a fairly satisfactory vacuum may be obtained. An improvement on this method can be effected by syruling hot as before, placing the lids loosely in position, passing the cans through a steam chest in which steam jets are allowed to impinge on the loose lids for fifteen to thirty seconds and then sealing immediately. This steam chest counteracts the effect of the cold lid, and is effective in replacing the air of the headspace by steam to a very large extent, but such methods are not entirely successful with fruits which contain a good deal of air in the tissues, as the whole process does not occupy sufficient time for this air to be driven off.

Hirst⁸ attempted to eliminate the exhaust tank by sealing the cans *in vacuo*, but was not able to obtain satisfactory results. He found, as just stated, that time is required to draw the air out of the tissues and that the short period during which the can was in the vacuum chamber before being sealed was not sufficient for this purpose. Hirst also attempted to combine vacuum-sealing with an exhaust, but found that if the cans were given the ordinary exhaust, and thus entered the vacuum chamber hot, the contents immediately boiled over. It was hoped that it might be possible to exhaust at a lower temperature and then seal under a partial vacuum, but it seems doubtful whether the method, even if satisfactory in other respects, would be sufficiently rapid for modern requirements.

Experiments at the Low Temperature Research Station, Cambridge, have shown that an advantage over the ordinary exhaust method is gained by combining this with the steam chest mentioned above. The lids are placed loosely in position

immediately the cans leave the exhaust tank, passed under the steam jets in the steam chest, and rolled on immediately. By this means the vacuum in the headspace may be increased by 2 or 3 inches, and the arrangement is such that the output need not be affected. Moreover, the cans go into the cooker at a higher temperature than they would with a low temperature exhaust coupled with the vacuum-sealing.

Another method of exhausting, which has been used for products like fish and meat, is to pass the cans through the exhaust tank with the lids clinched on but not rolled so as to make them airtight. The air thus escapes through the loose seam, which is made tight when the cans emerge. This method has an advantage in that the fruit at the top of the can is largely protected from the effect of steam and air as it passes through the tank, but it necessitates the installation of an additional machine for clinching the lids in position before they enter the exhaust tank, and may involve the crushing of any fruits which project above the tops of the cans. The damage from this cause, however, may not be serious enough to constitute an objection.

The old-fashioned method of exhausting by sealing the cans, heating them in the cooker, puncturing to allow air and steam to escape ("blowing"), and sealing again with solder ("tipping") is not used now for fruit, and is rapidly being superseded by other methods for fish, meat and vegetables.

Lidding and Sealing.

Lidding consists merely in placing the lid in position on the top of the can, and is usually carried out automatically by an attachment to the sealing machine. Reasons have already been given for carrying out this process earlier, i.e. either before the cans enter the exhaustor or between the exhaustor and a steam-box designed to heat the lids, thus improving the vacuum in the can.

Sealing.—Whether this is carried out automatically at a rate approaching 150 cans per minute, or whether it is carried out

with a small machine worked by hand, the principle of closure is the same. The outer edge of the lid and the flange at the top of the can are so hooked and rolled together, in two distinct operations by means of rollers specially grooved for the purpose, that a tight joint is made. This is facilitated by the fact that

the outer groove on the lid contains a thin layer of a jointing material, usually of rubber latex, applied in liquid form and subsequently dried. Paper gaskets, and even a paste prepared from gluten, have also been used for this purpose, but rubber* has proved by far the most reliable material from the point of view of checking small leaks. Considerable experience is required in adjusting the

rollers to make a perfect seam, but precise instructions for this purpose and the service of expert mechanics is always given by firms supplying automatic machinery.

* Rubber latex is used for this purpose in preference to vulcanised rubber, as the sulphur present in the latter is liable to cause blackening and promote corrosion.

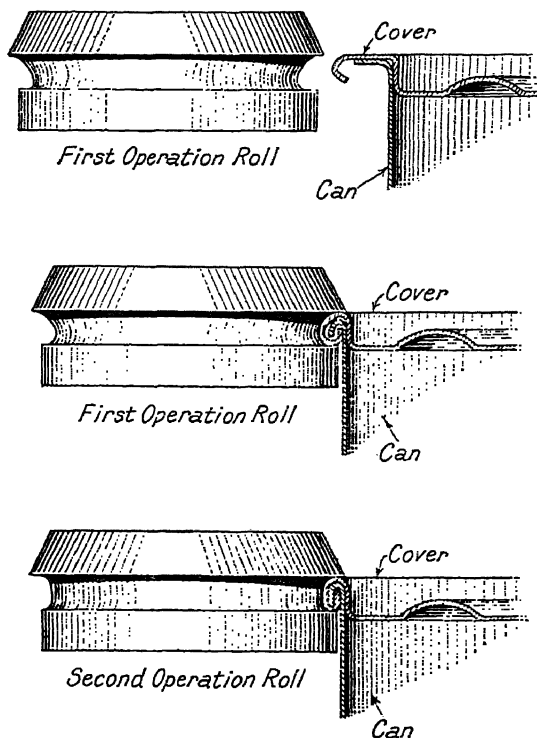


FIG. 11.—The seaming operation. [By the courtesy of the Editor of "Food Manufacture."]

Fig. 11 shows sections illustrating the type of seam formed and the rollers which produce it. Certain precautions and

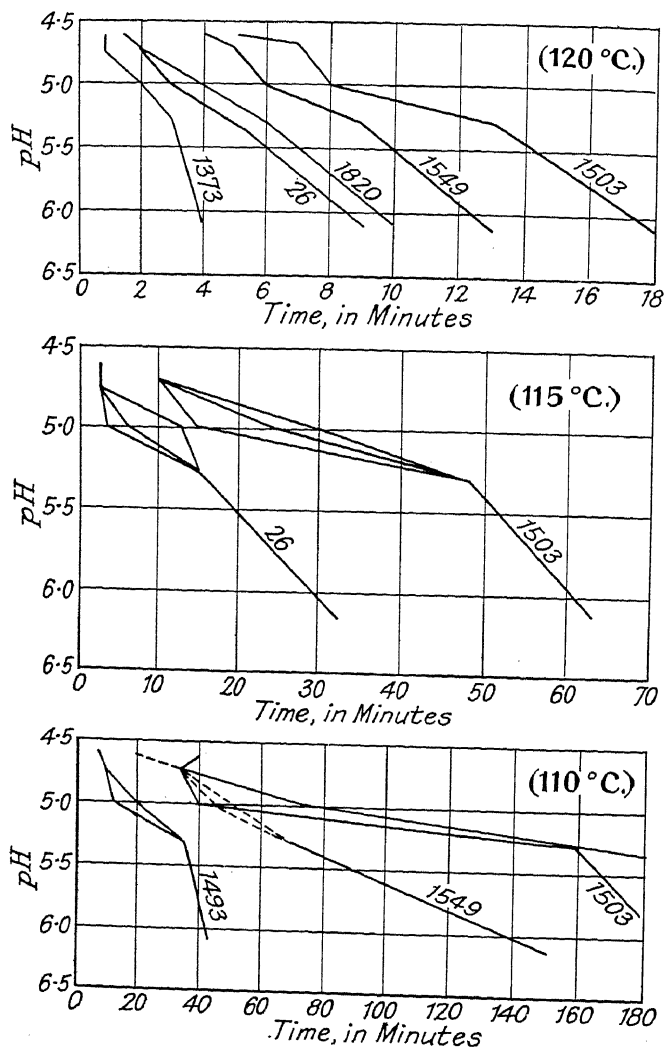


FIG. 12.—The influence of hydrogen-ion concentration on the time necessary to destroy spores heated at 110° C., 115° C., and 120° C. (after Bigelow and Esty).

The numbers on the curves relate to different strains of organisms.

GENERAL ACCOUNT OF THE PROCESSES

measurements of importance in obtaining a correct seam are as follows :—

- (1) The roller for the first operation must be adjusted so that it does not curl the cover flange too tightly or too loosely. In section the appearance after the first operation should be as in Fig. 11 (middle).
- (2) The roller for the second operation must compress the seam tightly. See Fig. 11 (bottom).
- (3) The countersink in the cover should be $\frac{1}{8}$ -inch deep.
- (4) The can hook under the cover hook should measure $\frac{1}{16}$ -inch.

It need hardly be stressed that since the success of the whole canning process depends on obtaining a perfect seal, too much care and watchfulness cannot be given to the sealing operation.

Processing Canned Fruits.

Processing or cooking canned fruits has for its object the destruction of bacteria and fungi which would otherwise cause spoilage.

With fruits this operation is rendered comparatively easy on account of the high acidity of the products ; with vegetables and meat it is much more difficult. The latter are subject to spoilage by thermophilic and other heat-resisting, spore-forming bacteria, among which is the well-known *Bacillus botulinus*. They must therefore be sterilised by heating in retorts at temperatures of 240° or 250° F. for a length of time sufficient to destroy such organisms. Fruits, on the other hand, are readily sterilised at the temperature of boiling water, or even lower.

Esty and Meyer have shown that the spores of *B. botulinus* rapidly lose their resistance to high temperatures in a medium which is on the acid side of p_H 4.5, as may be seen from Table XVI. Fig. 12, from Bigelow and Esty,¹⁰ also illustrates the effect of the H-ion concentration of the medium. Dickson, Burke and Ward¹¹ inoculated the well-washed spores of *B. botulinus* into canned peaches, pears and apricots, and

TABLE XVI.

FROM ESTY AND MEYER,⁹ "HEAT RESISTANCE OF SPORES OF *B. BOTULINUS* AND ALLIED ANAEROBES."

Effect of Heat on Spores of B. Botulinus suspended in Acidified Spinach Juice.

Hydrochloric Acid.				Citric Acid.			
p_H	Resistance at 100° C. in minutes.		Retarded Germination, days.	p_H	Resistance at 100° C. in minutes.		Retarded Germination, days.
	+	-			+	-	
<i>Control :</i>				<i>Control :</i>			
5.05	45	50	7	5.26	60	65	10
4.80	45	50	10	4.92	45	50	29
4.50	40	45	8	4.77	40	45	10
4.38	35	40	58	4.69	35	40	9
4.31	24	26	20	4.54	30	35	7
4.16	20	22	8	4.50	30	35	29
4.11	15	20	7	4.37	25	30	8
3.98	10	15	4	4.34	20	25	9
3.81	10	15	5	4.31	20	25	9
3.70	10	15	10	4.31	18	20	9

— = destruction time.

+ = survival time.

Note to Table XVI.

- (1) The long period during which germination is retarded in certain cases as the result of the heat treatment.
- (2) The p_H range found in canned fruits is from about 2.7 to 2.8 at the more acid end to about 4.5 at the less acid end.

poisoned guinea-pigs with the resulting juice. Esty and Meyer point out, however, that it is difficult to wash the spores entirely free from toxins, in fact, it is by no means certain that the disintegrated remains of the spores or vegetative forms of this bacillus are not in themselves poisonous; moreover, Dickson, Burke and Ward do not state whether the vegetative bacilli

were killed by heat. Esty and Meyer state that, as the spores are always subjected to heat in the course of the usual canning procedures, it is impossible to draw far-reaching conclusions from inoculation experiments conducted with unheated spore suspensions. Their own experiments indicate that de-toxified spores of *B. botulinus* do not find in acid products a favourable medium for growth, although they deem it advisable that rotten or worm-eaten pieces of fruit should be discarded. They state emphatically that "products with a p_H -value below 4.5 are not subject to botulinus spoilage when packed under proper sanitary conditions," but "all products with a p_H -value higher than 4.5 (as in canned vegetables, etc.), should be processed so that all portions of the can are heated sufficiently to destroy the most resistant strains of *B. botulinus*." No outbreak of botulism from *commercially* canned fruit has, so far as the author can find, been reported,* but a case of bacterial poisoning from canned apricots is reported by Savage,²² and a doubtful case with canned pears.

The incidence of cases of poisoning is, however, very low with commercially canned fruits as compared with other foods, and it is stated by Esty and Stevenson,^{12, 13} that "spoilage types in canned fruits appear to be limited to yeasts and to the non-sporing, mesophilic, facultative, anaerobic, acid-loving bacteria." "Flat sours," a type of spoilage caused by non-gas-forming thermophilic organisms in canned vegetables, have not been encountered in any acid products, nor has any spoilage directly attributable to spore-forming bacteria been observed. With products of low acidity (vegetables, etc.), it is often possible to diagnose cases of under-sterilisation from the fact that an examination of the contents of the cans nearly always reveals a pure culture of a bacterium, whereas with leaky cans a mixed culture is usually found. With fruits, on the

* Recently further trouble has been encountered with canned pears, and the case has been investigated by Meyer and Gunnison.¹⁶ The pears were *home-canned*.

other hand, diagnosis in this way is not possible, as there is likely to be a mixed infection in both cases.

Most of the non-sporing organisms found in fruits succumb in a few minutes to temperatures of about 60°C . ($= 140^{\circ}\text{F}$.), hence the cooking periods given in commercial processes are more than sufficient to ensure sterilisation. Figs. 13 and 14 (after W. D. Bigelow,^{14, 15}) show the effect of heating at different temperatures for different times on typical non-sporing organisms, such as might be found in canned fruits.

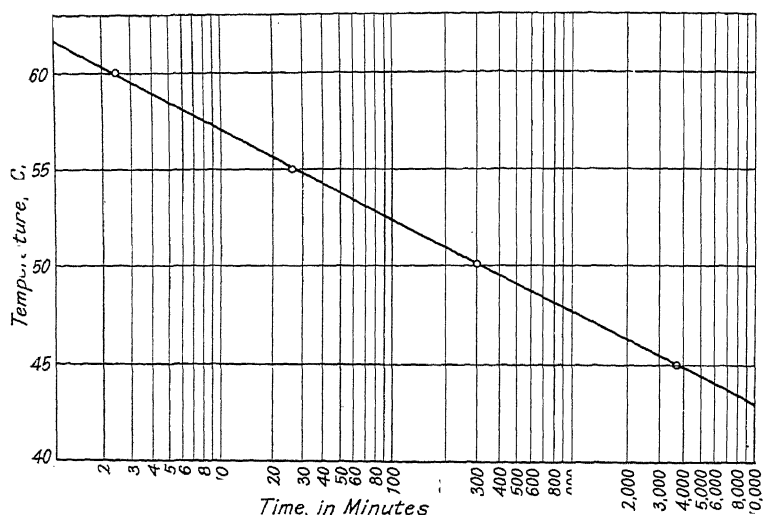


FIG. 13.—Average thermal-death-time curve of four non-spore-bearing organisms (after Bigelow).

Fig. 15 (also after Bigelow) shows, as a contrast, the results obtained with typical thermophilic organisms such as might cause spoilage in canned vegetables, meats, etc. It will be seen that, whereas in the Figs. 13 and 14 the highest temperature considered is 60°C ., in Fig. 15 it is 140°C .

In spite of the ease with which most organisms are killed in canned fruits, cases of under-sterilisation occasionally arise, especially with somewhat over-ripe canned apples and green-gages, and it is necessary to know something of the principles

involved in the penetration of cans by heat. These have been studied by Bitting,¹⁷ Magoon and Culpepper,¹⁸ and subsequently with more elaborate apparatus by Bigelow,¹⁵ who has worked chiefly with vegetables at high temperatures, although his work is equally applicable to other products. Bigelow regards the temperature at the centre of the can as the basis of any study of processing; he therefore studied the rate of heat-penetration to the centre of cans by means of a thermocouple which could be used for both stationary and rotating cookers.

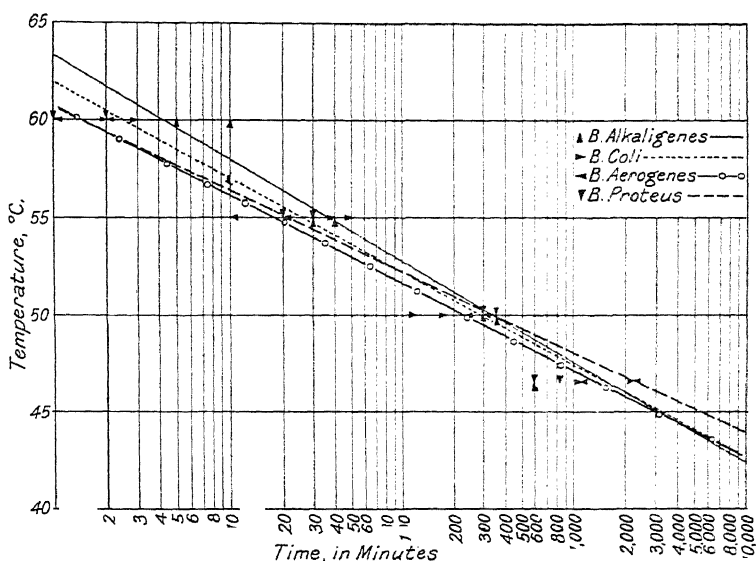


FIG. 14.—Logarithmic thermal-death-time curves (after Bigelow).

The following empirical rules were found to hold good :—

(1) The time necessary for heat to penetrate to the centre of cylindrical cans of different sizes, packed with the same product, is approximately proportional to the squares of the radii when the length of cans is greater than the diameter. Table XVII. showing the heat penetration for cans of different sizes, with the accompanying explanation, is based on actual tests carried out by Bigelow, and the figures obey the above law.

TABLE XVII.

HEAT PENETRATION THROUGH SOLIDLY PACKED PRODUCTS FOR CANS OF DIFFERENT SIZES.

Size of Can.	Factor for Obtaining Approximate Time for Cans of Specified Size.				
	No. 1.	No. 2.	No. 2½.	No. 3.	No. 10.
No. 1 .	1.0	1.7	2.3	2.5	5.4
No. 2 .	0.6	1.0	1.4	1.5	3.2
No. 2½ .	0.44	0.74	1.0	1.1	2.4
No. 3 .	0.41	0.68	0.9	1.0	2.2
No. 10 .	0.19	0.31	0.42	0.46	1.0

As an example of the use of this table, Bigelow takes the case of a No. 3 can of a given product which is processed at 250° F. with an initial temperature of 160° F., and in which the temperature at the centre reaches 220° F. after fifty-six

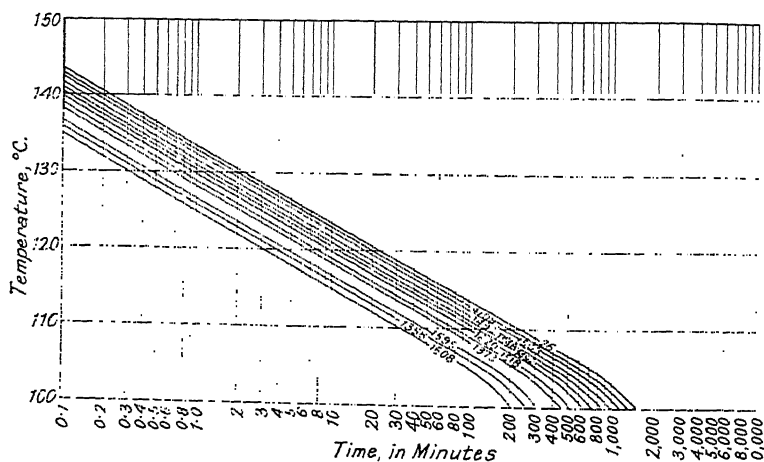


FIG. 15.—Logarithmic thermal-death-time curves of typical thermophilic organisms (after Bigelow).

minutes. The approximate time required to bring the centre of a No. 10 can of the same product with the same initial temperature to the same final temperature is found by multiplying 56 by the factor 2.2 shown in the last column of the table.

It is stated that these figures are especially applicable, in commercial practice, to products with very slow heat penetration, in which the transfer of heat is by conduction rather than by convection. With products that heat to the centre rapidly it is difficult to make the same comparison.

(2) If two cans of the same size and containing the same substance are heated to different temperatures and then placed in a cooker and processed together, the can with the lower temperature will heat faster than the other, so that the centres of the two cans will reach the temperature of the surrounding bath at approximately the same time. With products such as

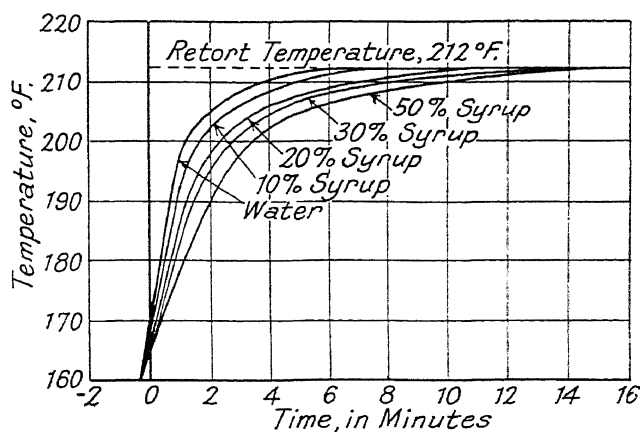


FIG. 16.—Heat penetration in water and syrups in No. 3 cans. Cans stationary (after Bigelow).

peas where heat passes quickly to the centre of the can, the initial temperature makes little difference to the sterilising process; this also applies to many fruits. With products like close-pack apples, in which heat penetration is slow, the initial temperatures matter a good deal, because it is the length of time at which the centre of the can is at high temperature which makes the process effective. Apples, therefore, should be filled into the cans while still hot from the preliminary steam-blanching.

(3) Heat penetration is most rapid with mobile liquids or with insoluble solids, surrounded by mobile liquids. The

addition of products which form a true solution, such as sugar or salt in concentrations used in canning fruits and vegetables, does not greatly retard heat penetration, although the effect may be appreciable (see Figs. 16 and 17). Products that soften when heated so that they pack together and also make the solution somewhat viscous, retard heat penetration. If the pieces of insoluble material are large like apples (loose-pack) or certain varieties of plums, they delay the heating of the liquor, which does not reach bath-temperature until all the pieces are heated to the centre. With products which pack

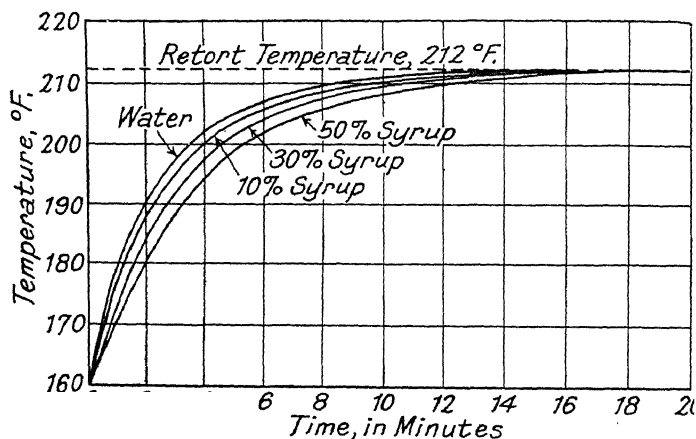


FIG. 17.—Heat penetration in water and syrups in No. 10 cans. Cans stationary (after Bigelow).

closely together and interfere with the movement of convection currents, conduction must take the place of convection, and heat penetration will be slow. Starch was found to retard heat penetration, as it renders the liquid viscous; doubtless other substances, like pectins and gums, act in a similar manner (see Fig. 18).

(4) Rotation or agitation greatly increases the rate of heat penetration with products containing large but movable masses like canned tomatoes or large plums, where there is some interference with convection currents. With products which consist of a clear liquid having small solid masses floating

freely in it, heat penetrates rapidly to the centres of the cans by means of convection currents, and rotation has less effect. Rotation also has very little effect with solidly packed products. Many of the modern types of cookers, however, are continuous, and the cans rotate slowly while passing through them. A

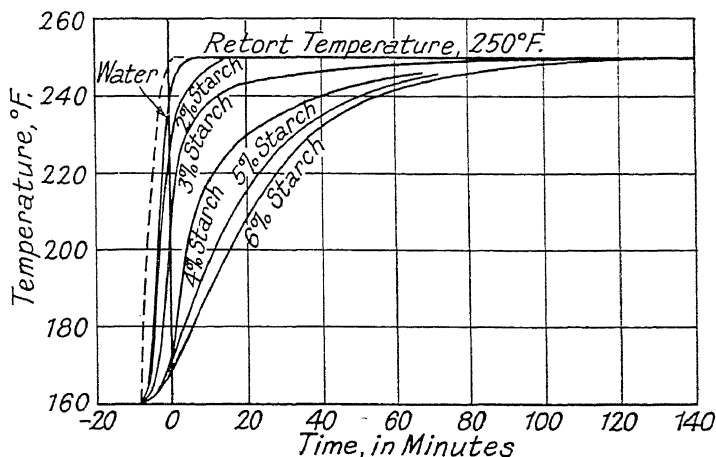


FIG. 18.—Heat penetration in water and starch solutions in No. 2 cans. Cans stationary (after Bigelow.)

serious drawback to the modern agitating cookers and coolers, which applies also to the run-ways along which the filled cans roll from place to place by gravity, is that delicate fruit is liable to become broken and lose its attractive appearance when turned out.

Cooling and Storage.

On emerging from the cooker, the cans are usually cooled to a temperature of about 110°-115° F. (or until the bulged ends of the cans resume their normal shape), by being passed through a continuous cooler in which water is used as the cooling medium. The can may either be immersed in cold water or sprayed and, in any case, a large supply of fresh, clean water is required.

Too little cooling results in "stack-burning," which involves

loss of colour and considerable corrosion of the can, and in any case it is not good policy to place the cans in large stacks immediately after cooling. On the other hand, if the cans are cooled below the temperature of the surrounding atmosphere, they remain wet and turn rusty. Moreover, if the seams are not perfectly tight, a little water may be drawn into the cans carrying infection with it when a vacuum begins to form inside. This does not occur to anything like the same extent when cans are cooled in a current of air, and for this reason air-cooling, although slower, might be regarded as preferable to water-cooling.¹⁹ It might be argued, however, that it is hardly good policy unduly to bolster up defects in can-making or seaming by "nursing" the cans at this stage in the manufacture. Kohman has ^{20(a)} recently drawn attention to the effect of slow cooling on the various reactions which bring about deterioration in the colour of canned fruits containing anthocyanin pigments. The rate of these reactions doubtless depends on temperature, hence Kohman ^{20(a)} has proposed that cooling be carried to a lower temperature than is usual in practice and, if trouble is experienced through the cans remaining wet, they should be dried by air currents. Kohman ^{20(b)} and the author ²¹ have also pointed out the advantage of artificial cool storage in protecting cans from corrosion and preserving the natural colours of the contents. This is an important point, and although it may not be practicable to keep cans in artificial cool storage, it may be considered as an axiom that warehouses should be made as cool, dry and well-ventilated as possible, and that cans should neither be packed in boxes nor stacked while still warm.

REFERENCES.

CANNING.

- 1 HIRST, F., and ADAM, W. B., "The Use of Sugar Syrups in Fruit Canning," *Canners' Bull.* No. 2, Univ. Bristol Res. Sta., Campden, Gloucestershire.
- "Varieties of Fruits Suitable for Canning," *Canners' Bull.* No. 3, Univ. Bristol Res. Sta., Campden, Gloucestershire.

- 2 BITTING, K. G., Bull. No. 10, Research Lab., Nat. Cannery Assoc., Washington, D.C., 1917.
- 3 KOHMAN, E. F., "Oxygen and Perforation in Canned Fruits," *J. Ind. and Eng. Chem.*, 1923, 15, 527.
- 4 ANON, "Canned Tomatoes and Tomato Products," Bull. 97A, Nat. Cannery Assoc., Washington, D.C.
- 5 BIGELOW, W. D., and STEVENSON, A. E., "Tomato Products," Bull. 21L, Nat. Cannery Assoc., Washington, D.C.
- 6 CRUESS, W. V., "Commercial Fruit and Vegetable Products," McGraw-Hill Book Co. Inc., 1924.
- 7 MORRIS, T. N., and BRYAN, J. M., "Standardisation of Canned Fruits," *Food Manufacture*, 1931, 6.
- 8 HIRST, F., *Food Manufacture*, 1930, 5, 326.
- 9 ESTY, J. R., and MEYER, K. F., "Heat Resistance of Spores of *B. botulinus* and Allied Anaerobes," *J. Inf. Dis.*, 1922, 31, 650.
- 10 BIGELOW, W. D., and ESTY, J. R., "Thermal Death-Point in Relation to Time of Thermophilic Organisms," *J. Inf. Dis.*, 1920, 27, 602.
- 11 DICKSON, BURKE and WARD, *Arch. Int. Med.*, 1919, 24, 581.
- 12 ESTY, J. R., and STEVENSON, A. E., "Examination of Spoiled Canned Foods," *J. Inf. Dis.*, 1925, 36, 486.
- 13 CAMERON, E. J., and ESTY, J. R., "Examination of Spoiled Canned Foods," *J. Inf. Dis.*, 1926, 39, 89.
- 14 BIGELOW, W. D., *J. Inf. Dis.*, 1921, 29, 528.
- 15 — "Heat Penetration in Processing Canned Foods," Bull. No. 162, Nat. Cannery Assoc., Washington, D.C.
- 16 MEYER, K. F., and GUNNISON, J. B., "Botulism Due to Home-Canned Bartlett Pears," *J. Infect. Dis.*, 1929, 45, 135.
- 17 BITTING, A. W., "Exhaust and Vacuum," Nat. Cannery Research Lab., Bull. No. 8.
"Processing and Processing Devices," *ibid.*, No. 9.
- 18 MAGOON, C. A., and CULPEPPER, C. W., "A Study of the Factors Affecting Temperature Changes in the Container during the Canning of Fruits and Vegetables," U.S. Dep. Agric. Bull. 956.
"Relation of Initial Temperature to Pressure, Vacuum and Temperature Changes in the Container during Canning Operations," U.S. Dep. Agric. Bull. 1022.
- 19 HALLMAN, G. V., and STEVENS, R. G., "Sterilizing Canned Foods," *Ind. and Eng. Chem.*, 1932, 24, 659.
- 20(a) KOHMAN, E. F., "Shortcomings of Cooling Equipment for Fruit Cannery," *The Fruit Products Journal*, 1931.
- 20(b) — "Storage Temperatures for Canned Fruits," Nat. Cannery Assoc., Bull. No. 23L.
- 21 "The Corrosion of the Tinsplate Container by Food Products," F.I.B. Special Report No. 40. H.M. Stationery Office, 1931. 1s. 6d. net.
- 22 SAVAGE, W. G., and WHITE, P. B., "Food Poisoning; A Study of 100 Recent Outbreaks," Rep. of Med. Res. Council, 1925, pp. 110, 111.

CHAPTER V.

SPOILAGE.

SPOILAGE of canned goods may be due to the following causes :—

- (a) Growth of micro-organisms such as moulds, yeasts or bacteria, present either through under-sterilisation or leaks.
- (b) Corrosion of the tin or iron of which the can is made resulting in discoloration of the contents and in the formation of hydrogen swells and perforations.
- (c) Over-filled, dented or rusty cans.

Sterilisation and processing have already been considered (pp. 99-107); discoloration is discussed in the section on fruit colours, and the items in section (c), which are due to carelessness, defective machinery or bad storage conditions, involve questions of management, etc.,* which, although of the greatest importance in practical canning, are very largely outside the scope of this book. There remains the corrosion of tin-plate, which is of considerable importance, especially in warm climates, and which has received much attention from research workers, especially in America.

A review of the literature on this subject has been made in the Food Investigation Board Special Report, No. 40, issued by the Department of Scientific and Industrial Research.¹ This

* Cases have come to the author's notice in which external corrosion has been brought about mainly through damage to the external tin-coating in soldering (by the use of an unsuitable flux), and by de-tinning through the cans having been processed at high temperature in a bath of calcium-chloride brine.

report, together with the Annual Reports of the Food Investigation Board⁹ from 1928 onwards, describe the researches at the Low Temperature Research Station at Cambridge, and the following account is largely based upon these sources.

The early work on corrosion in canned foods was much concerned with the quantity of tin to be found in them, and some of this has been summarised in the Report of the Inspector of Foods for the Local Government Board in 1908, which also contains a discussion on the toxicity of tin. The figures given in this report show that the amount of tin dissolved from tin-plate bears little relation to the acidity of the product canned : it is, in fact, highest in some products of low acidity.

Hall, and later, Kohman, showed that access of oxygen to the contents of a can renders the tin liable to attack. Kohman, Culpepper and others also noted a similar effect with reducible substances, such as anthocyanin pigments. Conversely Hall, Chapman, Lehmann, Coerbergh, De Fouw and the authors of the F.I.B. Report have all shown that tin is not attacked appreciably by organic acids in the absence of oxygen, an immunity which, in the opinion of many workers, it owes to the high overvoltage of hydrogen on its surface.

Bigelow and Goss noticed that the dissolved tin is not evenly distributed between solids and liquids in canned foods, but preponderates greatly in the former, where it is deposited mainly in an insoluble form.

With regard to the toxicity of tin, it is now generally recognised that there is very little danger from tin poisoning, as the result of eating canned foods. Rossee and Morgenstein have pointed out that the greater part of the tin in canned foods is in an insoluble form, which is not acted upon by the gastric juice and therefore not assimilated. The statutory limit for tin has, however, been set at 2 grains per pound of food, a quantity which is rarely exceeded. Such caution is, on the whole, wise in the present state of knowledge, since it cannot be definitely stated that small amounts of tin are entirely without effect on metabolism, and for this reason it is desirable to take measures

to keep the amount of tin which may gain access to food as low as possible.

Hydrogen Swells and Perforations.

Hydrogen swells are caused by the formation of hydrogen in cans by the action of the fruit acids on the tin and iron of which the can is made. When this attack is concentrated at certain spots, so as to cause pitting, the can may actually become perforated. Hydrogen swells may be found in all stages from "springers" or "flippers" to tightly-bulged cans which seem almost on the point of bursting, and, although the contents are not necessarily harmful, such cans are unsaleable because the same external appearance is seen in the early stages of fermentation. Hydrogen swells may occur with both plain and lacquered cans, but, curiously enough, more trouble is usually experienced with the latter; even cans which have been twice lacquered inside are by no means immune. It is also remarkable that the greatest trouble is often experienced with fruits of low acidity, especially fruits in syrup in which the p_H ranges from about 3.5 to 4.5. Sweet cherries of all colours, but more especially the darker ones, "ready-to-serve" prunes and bilberries are notable examples of products which give rise to hydrogen swells and perforations, but more or less severe losses may also be encountered with greengages, strawberries, rhubarb, blackberries, grape-fruit and loganberries. Gooseberries, pineapples and tomatoes rarely give trouble, and peaches, pears and apricots* are also generally immune.

Examination of the insides of plain cans which have become hydrogen swells usually reveals large de-tinned areas, although there are exceptions to this rule (see p. 128). With lacquered cans there is often little visible damage, and, on the whole, mere inspection throws little light on the subject, because

* The absence of trouble with these fruits may be due largely, as Kohman has pointed out, to the fact that they are almost always packed in plain cans.

normal cans often appear to be quite as badly corroded as those which have become hydrogen swells.

Perforations are much less common than hydrogen swells, but may sometimes cause losses with highly coloured fruits and with dried prunes, which have been canned in syrup. They are also seen occasionally with strawberries and apples, and, as in the case of hydrogen swells, lacquered cans give more trouble than unlacquered, and fruits of low acidity more trouble than fruits of high acidity.

In the early researches on hydrogen swells and perforations, actual canning experiments were carried out on a large scale, and although valuable results were obtained by Culpepper, Kohman and others as regards the influence of oxygen and reducible substances such as the fruit colouring matters in increasing the incidence of these troubles, the method, if applied to every case, would have been extremely cumbersome, and the results slowly obtained. Moreover, little light was thrown on the more fundamental aspects of the problems.

More recently Kohman and Sanborn, Lueck and Blair and others began to study the subject from the point of view of the relative potentials of tin and iron in couple in various acid media, and the effect of one metal on the rate of corrosion of the other. It was noticed that the iron was initially anodic to the tin, but that a reversal of potential quickly occurred in which the iron became the cathode and the tin the anode. In other words, iron was initially the corroding member of the couple, but soon this rôle appeared to be taken over by the tin. Lueck and Blair ascribe this change to the high over-potential of hydrogen on tin which causes the iron to be the only avenue of escape for the hydrogen, so that a back E.M.F. results.

These findings have been confirmed, in the main, at Cambridge by Morris and Bryan,^{1, 9} but there appeared to be certain almost insuperable difficulties in attacking the problem along these lines. For instance, it was found that the change in potential was exceedingly rapid when contact between the two metals was broken in order to take measurements, especially

after prolonged immersion. The same difficulty was noticed by Lueck and Blair, and it would appear that, however rapidly the readings which can be obtained by this method are taken, they greatly exaggerate the magnitude of any reversal of potential which may have occurred, and that, in reality, after prolonged immersion the current flowing between the two metals is very minute ; indeed, it proved too small to give an appreciable reading with a sensitive milliammeter. Although there seems no doubt, however, that tin gives considerable electrochemical protection to iron, no measurements of this kind bear any relation to the relative rates of corrosion of the two metals, since although the iron may be acting as cathode to the tin in the couple, it is itself corroding by local action.

Kohman and Sanborn noticed a powerful inhibiting effect of tin salts on the corrosion of iron, and, in experiments with tin and iron in couple, they showed that the rate of attack on tin, per unit area, by an acid medium increased with the area of iron exposed. On the other hand, an increase in the area of tin decreased the attack, per unit area, on both metals.

In their latest publications on this subject, Kohman and Sanborn emphasise the observations of Bigelow and Goss in connection with the removal of tin from solution by the solids of the fruit, particularly the proteins, and believe that tin being anodic to the iron gives electrochemical protection which is most pronounced at high acidity. This protection is considered to be much greater with plain cans in which the area of tin is very large in proportion to that of the iron, than in lacquered cans where the two metals are fairly equally exposed. In lacquered cans removal of any exposed tin is more rapid than in plain ones and, since the dissolved tin is absorbed by the solids, it is unable to exert its inhibiting action on the corrosion of iron, which can therefore proceed unchecked.

If it be true that increase in the acidity of the corroding medium decreases the nobility of the tin in tin-plate relatively to that of the iron, there is, clearly, a danger that the tin-coating will be removed most rapidly at high acidity and allow

corrosion of iron and formation of hydrogen to proceed apace. This danger is well defined by U. R. Evans ² as follows : " The choice of a metal to form a protective covering on iron will depend on the following conditions : (1) If there is any fear that the coating will become cracked or scraped away, the metal chosen must be anodic to iron, and must be capable of conferring on the iron at the points exposed a cathodic current density exceeding the minimum value needed for protection. But, since this current is generated through the anodic corrosion of the covering metal, the minimum value should not be unduly exceeded or the covering will have a short life. . . . "

It has already been stated that fruits of low acidity often form hydrogen swells more quickly than those of higher acidity, and experiments by Mrak and Richert,⁴ by Hirst and Adam,³ by Kohman and Sanborn,⁵ and by Morris and Bryan ¹ have shown that the addition of acid to certain fruits such as canned dessert cherries, canned dried prunes,* greengages and bilberries † is beneficial in retarding the rate of occurrence of losses due to corrosion.

If Kohman and Sanborn's explanation given above is correct, it means that at the normal acidity of these fruits the tin is not sufficiently anodic to the iron to be protective, or it may even be slightly cathodic. The addition of a *small amount* of acid, however, would cause the cathodic current density in the iron to reach the " minimum necessary for protection." It has been further shown by Culpepper and co-workers that media of *very* high acidity (2-5 per cent. of citric acid) cause rapid formation of hydrogen swells or perforations : in other words, the " necessary minimum " is exceeded.

The explanation favoured by Morris and Bryan ¹ in their report is based on the fact that increase in acidity does *not*, under all conditions, increase de-tinning, but that the relative

* Mrak and Richert ⁴ state that the colour of these is adversely affected by the addition of acid, but in the Author's experiments this did not appear to constitute an objection unless the amount added was excessive.

† Blackberries seem to be an exception to this rule according to experiments by Hirst and Adam.³

attack on the two metals at different hydrogen-ion concentrations is also affected by such factors as the relative areas of each exposed, and the amount of oxygen present. Thus, if strips of tin-plate, in which tin and iron have been equally exposed, are placed in solutions containing citric acid buffered with sodium citrate in the absence of air, tin is attacked more rapidly at low than at high acidity. There is, in fact, a well-marked increase in de-tinning from p_H 2.4 to p_H 5 which is easily perceptible to the eye, although this state of affairs is gradually reversed with increasing concentration of oxygen until, finally, de-tinning becomes most rapid at high acidity. If we assume that there is any parallel between the action of fruit juices and the simple buffered solutions, we see from this that, in lacquered cans, where the areas of tin and iron exposed (through scratches and other defects) are, in all probability, fairly equal, whether de-tinning takes place most rapidly at high or at low acidity depends largely on the supply of oxygen available.

It has further been shown by Morris and Bryan that the inhibiting efficiency of both tin salts and organic inhibitors of corrosion is less at low than at high acidity, whilst, according to Culpepper and Caldwell,⁶ and Leach,⁷ the absorption of tin by fruit solids and the formation of insoluble tin compounds is probably greater. There are, therefore, factors at low acidity which make for de-tinning, whereas at slightly higher acidities the metal may enjoy a certain measure of protection.

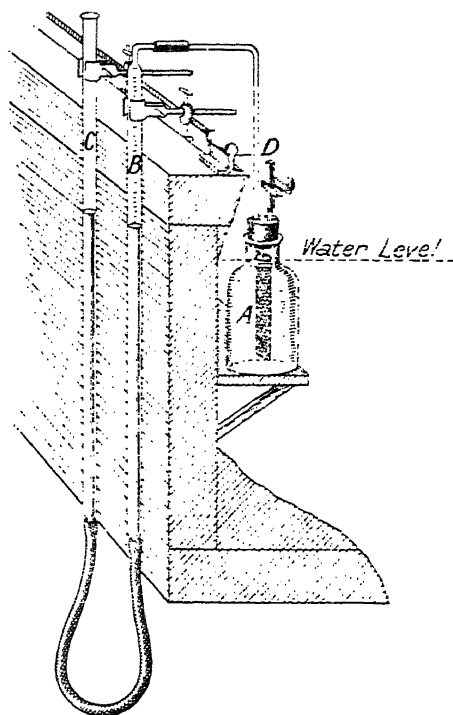
It has already been stated that hydrogen-swells occur most frequently with lacquered cans. This is ascribed to the fact that, with these, the iron enjoys less electrochemical protection than with plain cans, but in spite of this tendency it is often observed in practice that very severe de-tinning of plain tin-plate occurs with products of low acidity such as canned dried prunes, and certain vegetables and meats, whereas more acid products, like gooseberries, often show comparatively little. Such de-tinning may sometimes be sufficient to account for most of the hydrogen produced in corrosion, and the quantity of iron dissolved from the can may be insignificant. In other words,

with plain cans (except in the special case of highly acid products contaminated with sulphur, p. 127), de-tinning may be an important factor in the production of hydrogen.

Taking all things into consideration, it seems that, although acidity undoubtedly influences the attack on the metal with

fruit juices as well as with simple solutions, the particular hydrogen-ion concentration at which the formation of hydrogen swells and perforations takes place most rapidly depends on a large number of factors, and may, possibly, be almost specific for each canned product. How numerous these factors are may be readily gathered from literature on the subject, including the F.I.B. Special Report No. 40, and the Annual Reports of the Food Investigation Board already referred to. Among the researches described in the latter are the effects of surface

differences in the metals, of variations in the steel-base of tin-plate, of oxidising agents and oxygen on the corrosion of iron and tin, of the products of corrosion on each other, and on the further corrosion of the metals, of variations in acidity and of accelerators and inhibitors of corrosion, including sulphur



- A. Corrosion vessel.
- B. Gas measuring tube.
- C. Levelling tube.

FIG. 19.—Vertical section through thermo-static bath, showing the apparatus used in studying the rate of corrosion of metal strips (after Morris and Bryan).

compounds and beet sugar respectively, and until these closely interwoven factors can be fully investigated and correlated, all theories put forward to explain the phenomena of the corrosion of tin-plate by canned foods must be regarded as somewhat tentative.

At the risk of some repetition of what has already been written, the following account of the work of the Food Investigation Board will not be out of place here. In this work Morris and Bryan have endeavoured to imitate in glass vessels the conditions prevailing in a can, and to study the effect of the numerous factors likely to affect the corrosion of tin-plate by fruit acids either singly or in any desired combination.

The apparatus used (see Fig. 19) consists essentially of a glass bottle, containing metal test-piece and corroding medium and attached to a gas burette and levelling tube filled with mercury. The bottle is held at constant temperature in a thermostat, and the corrosion is followed by readings of the gas burette, and finally estimated by observing the loss in weight of the test-piece. The apparatus is thus a closed system, like a can, in which corrosion is taking place and is capable of considerable adaptation since the headspace in the bottle may be varied in size and evacuated and filled with nitrogen or any other gas, which can be analysed after a test. Also it is possible by simple modifications to use the same arrangement for the tin-iron couple.

The Corrosion of Mild Steel and Tin not in Couple.

In testing mild steel in different stages of manufacture, it was found that, in the particular samples examined, the *cold rolling* process appeared to have the greatest influence in slowing down the rate of corrosion by dilute citric acid. It has further been shown that different sheets of "white annealed" steel base, and even different portions of the same sheet, often vary greatly in the rate at which they undergo attack by fruit acids. These variations are also apparent when steels which

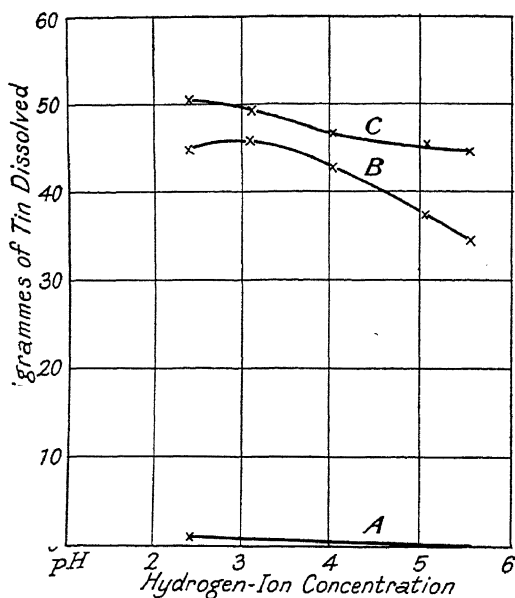
corrode at different rates are coupled with tin, hence it seems likely that they will be found to have considerable influence on the corrosion of tin-plate. It is hoped that further study will enable the variations to be traced to some definite treatment which the metal has received in the course of manufacture, so that it will be possible, ultimately, to control the steel base in such a manner as to increase its resistance to corrosion.

A thorough investigation of the various factors, external to the metals, which affect the rates of corrosion of iron and tin by citric acid have been carried out. The chief of these so far studied are the hydrogen-ion concentration of the corroding medium, the presence and absence of air or oxidising agents, and the effect of the corrosion products, i.e. the salts of the two metals, on further corrosion. This work has been undertaken because it was felt that the ways in which the separate metals respond to these factors are closely interwoven with their behaviour when coupled together as in tin-plate.

In studying the effect of hydrogen-ion concentration, solutions containing 5 grams of citric acid per litre were buffered with sodium citrate over the p_H -range 2.4 to 5.5. In the absence of air the rate of corrosion of *steel* decreased rapidly with decreasing acidity: in the presence of air it was little affected at high acidity, but there was a marked increase at low acidity which greatly reduced the general slope of the corrosion-acidity curve. It also seems fairly certain that organic oxidising agents present in foodstuffs act in much the same way as oxygen. The activity of oxygen as an agent in promoting the corrosion of iron has further been shown to be greatly increased by the salts of that metal in solution. These are capable of acting as oxygen carriers, especially at low acidity, and it seems more than probable that the phenomena of pitting and perforation which occur, especially at low acidity (the neighbourhood of p_H 4), are connected with oxidation.

In this connection it was noticed that when oxygen was present, even in the smallest traces, variation in the hydrogen-ion concentration of the corroding medium had a curious effect

in altering the point of attack of the acid on the steel. At p_H 2.4 and 3.1, corrosion was mainly confined to the edges of the strips, at p_H 5.0 and 5.5 it was confined to the middle regions, the edges being unattacked, whilst at p_H 4 there was a transition between these two conditions. It appears from this that exposed portions of the steel tend to be attacked at high



- A. In the absence of air.
 B and C. In the presence of a limited supply of air.
 B. Period of corrosion, 10 days.
 C. Period of corrosion, 28 days.

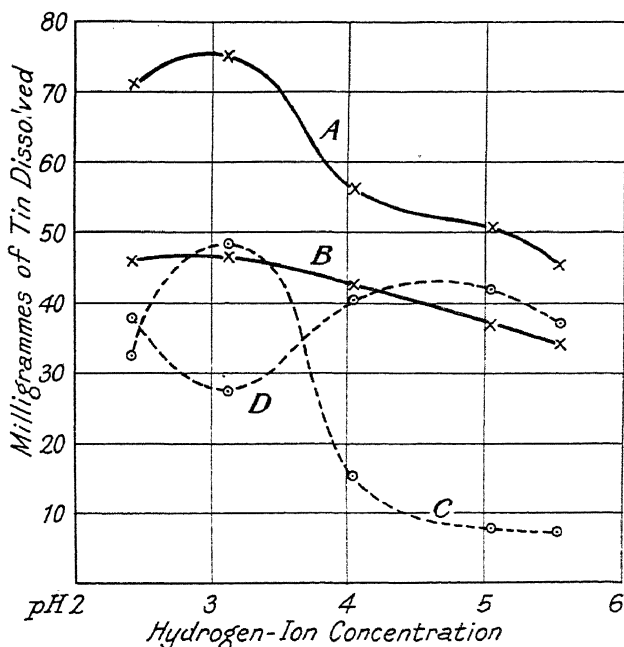
FIG. 20.—Corrosion of tin by citric acid at different hydrogen-ion concentrations (after Morris and Bryan).

acidity: at low acidity less exposed portions are attacked, a condition which would again favour pitting and perforation.

Tin is not attacked by non-oxidising organic acids in the absence of oxygen to any measurable extent. In the presence of oxygen or substances like salts of iron, which can act as oxygen carriers, it is attacked most rapidly at high acidity (see Figs. 20 and 21 representing, respectively, the corrosion of tin

by citric acid in the presence and absence of air, and its corrosion by citric acid in the presence of air and ferrous citrate).

Change in acidity also affects the equilibrium between stannous, stannic, ferrous and ferric salts, the extent to which hydrogen is either depolarised or evolved and the extent to which



- A. Corrosion for a period of 10 days ; ferrous citrate and air present.
- B. Corrosion in the absence of ferrous iron for 10 days (for comparison).
- C. Quantity of dissolved tin in the stannous condition.
- D. Quantity of dissolved tin in the stannic condition.

FIG. 21.—Corrosion of tin in the presence of definite amounts of air and ferrous citrate at different hydrogen-ion concentrations (after Bryan).

the organic acids or other organic substances are themselves oxidised.

The Tin-iron Couple and Tin-plate.

Allowing for somewhat different conditions, the corrosion of the tin-iron couple and tin-plate are similar. Tin-plate is to be regarded as a special case of the tin-iron couple in which

the tin is present in limited amount, but covers a very large area as compared with the iron. Hence, although the couple-effect may be somewhat small at first, it may increase rapidly as the thin tin coating is removed.

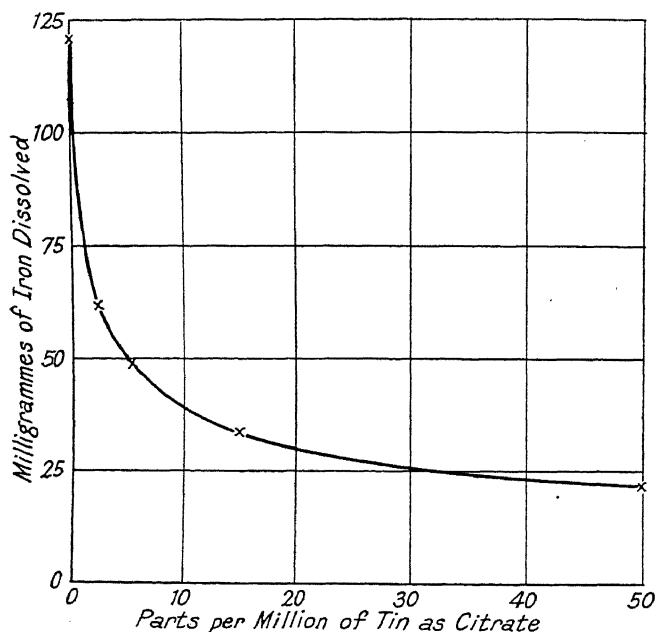


FIG. 22.—The effect of increasing quantities of tin as citrate on the rate of corrosion of iron by a 0.5 per cent. solution of citric acid over a given period (*after Morris and Bryan*).

The chief properties of tin and iron, either in the same solution or in actual couple, are as follows :—

1. The mere presence of tin in the same solution as iron (without contact) has a great influence in slowing down the corrosion of the latter : * this is much more marked when the two metals are in contact. The former effect is probably due to the inhibiting power of traces of tin salts in solution (see Fig. 22) on the corrosion of iron.

2. Tin is slowly dissolved by fruit acids when in contact with iron, even in the absence of air, the attack on it under

* Kohman (see p. 133).

these conditions being greatest at low acidity while the attack on the iron is greatest at high acidity. If the quantity of air present is increased, the acidity at which the most tin dissolves gradually changes and, no matter what the relative areas of tin and iron exposed may be, we pass from a condition in which the attack is greatest at low acidity to one in which it is greatest at high acidity. In other words, the acidity at which tin is removed most rapidly from tin-plate depends upon the quantity

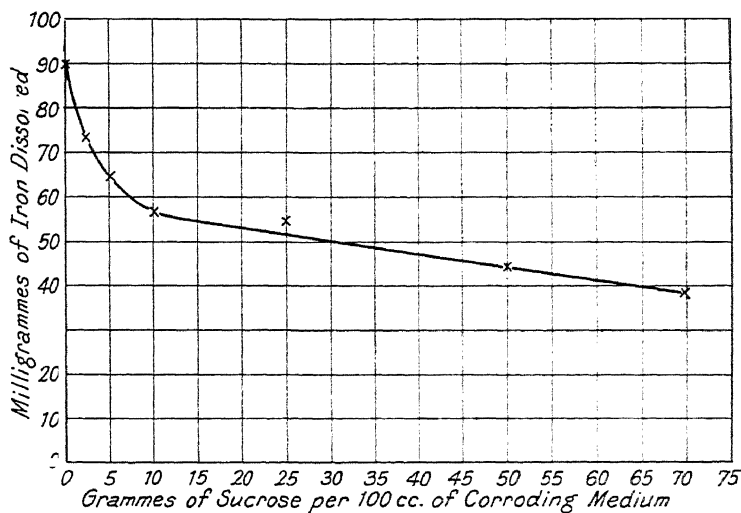


FIG. 23.—The effect of increasing quantities of pure sucrose on the rate of corrosion of iron by a solution containing 5 grams of citric acid per litre over a period of 4 days (after Morris and Bryan).

of available oxygen present in the material to which the tin-plate is exposed.

3. The hydrogen replaced from the acid by the dissolution of both the tin and iron is evolved from the surface of the iron—so that all the gaseous hydrogen comes from the iron surface. This is due to the high over-potential of hydrogen on tin. Even in couple no appreciable quantity of tin would go into solution were it not for the fact that the iron provides an avenue for the escape of hydrogen.

4. There is a reversal of potential after immersion of the

tin-iron couple in acid solution. Initially the iron is the anode (the corroding metal), but in a very short time the current is reversed and the tin appears to be the anode. This has already been referred to (p. 113), but it may be added here that it must not be thought that, because the tin is apparently the anode, it is the only metal which is corroding: the iron may really be corroding at the same time faster than the tin through the action of local couples.

5. It is almost invariably observed that when, for any reason, the corrosion of the tin member of the couple is diminished, the corrosion of the iron shows a corresponding increase, and *vice versa*.

The rate of de-tinning is considered to be a factor of first importance in governing the corrosion of tin-plate, since, after the tin has been removed from the plate and thrown out of solution by hydrolysis or by absorption into the solids of the foodstuff, or by combination with pigments, etc., the iron is free to be attacked by acids with liberation of hydrogen.

It has already been shown that the rate of de-tinning depends especially on factors such as the acidity and the available oxygen present, and it may well prove to be true that each product has an acidity which most favours the formation of hydrogen swells and perforations, and that a change in one direction or the other may result in a reduction of these. For instance, it has been shown at Cambridge and elsewhere that cherries, prunes and greengages form hydrogen swells less rapidly when the acidity is increased, but cases are reported with other fruits³ in which the addition of acid has done harm. It is hoped that more data will be gained on this subject in course of time, but meanwhile, if trouble is experienced with products when exported to hot countries, the possibility of benefit arising from a slight adjustment of acidity should be borne in mind. In any case, the foregoing remarks all point to the paramount importance of removing as much oxygen as possible from the headspace and contents of cans by means of an efficient exhaust.

Inhibitors and Accelerators of Corrosion.

The possibility of accelerators or inhibitors of corrosion having an effect in canning has been very largely neglected ; it is a fact, however, that many organic compounds with large molecules, and also some colloidal substances, are known which inhibit the acid corrosion of iron by slowing down or preventing evolution of hydrogen from cathodic portions of the metal. Some of these substances are very efficient, and are used commercially as " restrainers " in pickling baths for the removal of oxide films : they prevent or retard metal from going into solution, but do not interfere with dissolution of the oxide.

Other substances, such as sulphur in the form of sulphur dioxide or hydrogen sulphide, accelerate corrosion in acid solutions under certain conditions (see below).

The chief results with *inhibitors* which were obtained at the Low Temperature Research Station are as follows :—

(i) Beet sugar has been found to contain an inhibitor of the corrosion of iron. This is present as an impurity in the beet sugar, and is not due to sucrose itself, which is only a weak inhibitor. Crude beet sugar contains much more inhibitor than refined.

(ii) Beet sugar and agar-agar have been shown to have a definite protective action on both the iron and tin of tin-plate at all hydrogen-ion concentrations met with in canning, but it is doubtful whether agar could be used in practical canning owing to its tendency to form a jelly even at low concentrations.

(iii) Although sugar derived from the cane does not ordinarily exhibit more than slight inhibiting properties, inversion by heating a solution of cane-sugar with acid causes an inhibitor to be formed.

The effect of these inhibitors in canning has not yet been worked out,* but the value of a number of factors tending to lessen corrosion should not be neglected. Cannerymen and others

*Recent work by Hirst and by the Author has shown a definite benefit resulting from the use of sugars containing inhibitors in canning certain acid products.

who wish to test the respective merits of cane and beet sugars with their various products are warned, however, that there is much indiscriminate mixing of these at the present time, and

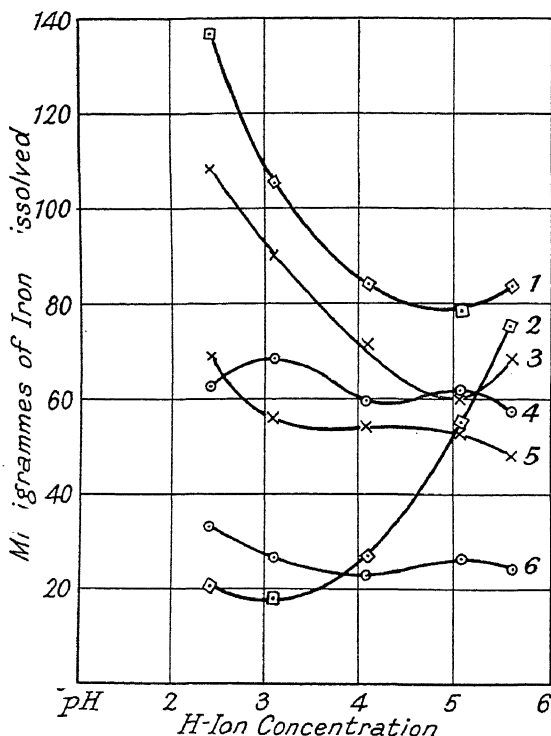


FIG. 24.—The effect of hydrogen-ion concentration on the efficiency of various inhibitors of the corrosion of iron (*Ann. Rep. F.I.B.*).

1. Standard curve for the corrosion of iron by solutions containing 5 grams of citric acid per litre buffered over the pH range with sodium citrate.
2. Curve with similar solutions + 0.5 per cent. of gelatin.
3. " " " " + 0.5 per cent. of pectin.
4. " " " " + 4 parts per million of tin as citrate.
5. " " " " + 25 per cent. of sucrose.
6. " " " " + 25 per cent. of crude beet sugar.

Note.—The period of corrosion in each case was 3 days, except in No. 6 (9 days). All the curves except No. 3 depart more from the normal at high than at low acidity.

that it is often difficult or impossible for a dealer to guarantee that any given sample is not so mixed. The sugars intended for large-scale tests should therefore be compared before use

for their effect on the corrosion of iron, since this provides evidence of the presence or absence of inhibitors, the value of which it is desired to estimate.

An important fact in connection with the action of inhibitors (or accelerators, as will be seen later), is that their efficiency alters considerably with variation in hydrogen-ion concentration. Generally speaking, they are most efficient at high hydrogen-ion concentration. Thus, gelatin was found to be a very powerful inhibitor at p_H 2.4, but its inhibiting effect was negligible at p_H 5.5. This was the most outstanding case tested, but the phenomenon was also seen with tin salts, beet sugar, and even with sucrose itself (see Fig. 24). This diminished effectiveness of inhibitors at low acidity may well be another reason why fruits of low acidity give the most trouble.

Other interesting features connected with inhibitors are :—

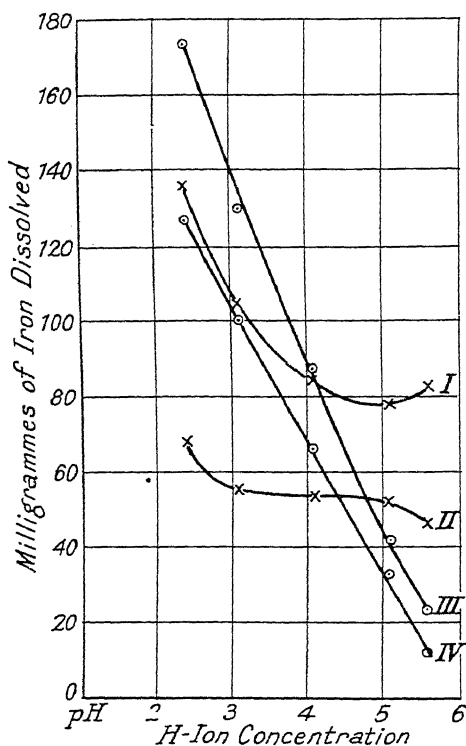
1. They often act when present in very small quantities, e.g. two parts per million of tin as citrate halved the rate of corrosion of iron in a 0.5 per cent. citric acid solution (Fig. 22).

2. Although small quantities of an inhibitor are effective, after a certain concentration is reached the addition of more has relatively little effect (Figs. 22 and 23).

As regards *accelerators*, interesting results have been obtained in studies on the effect of traces of sulphur, as sulphur dioxide or hydrogen sulphide in the citric acid solutions, on iron and tin-plate. With *iron alone*, a few parts per million of sulphur dioxide was found to accelerate corrosion at p_H 2.4, but actually retarded it at p_H 5 and 5.5. At p_H 4 the effect was negligible (Fig. 25). With sugar present, the accelerating effect of sulphur on the corrosion of iron at the acid end of the p_H -range studied was even more marked, and at the more alkaline end retardation was again seen (Fig. 25).

With *tin-plate*, sulphur dioxide gave remarkable protection to the tin at the more acid end of the series, but a great deal of iron was dissolved. At the less acid end the tin was protected, less than at high acidity, and the rate of corrosion of iron was comparatively slow. A brown stain of tin sulphide could

be seen on the tin, especially at the more acid end of the p_H -range, and it seems highly probable that this forms a



- I. Control curve with buffered solutions containing 5 grams of citric acid per litre.
- II. Control curve with similar solutions + 25 grams of sucrose per litre.
- III. Solutions as in I. + 16 parts per million of sulphur dioxide.
- IV. Solutions as in II. + 16 parts per million of sulphur dioxide.

FIG. 25.—The accelerating effect of sulphur dioxide on the rate of corrosion of iron over the p_H -range 2.4 to 5.5 (*Ann. Rep. F.I.B.*).

Note—The accelerating effect of sulphur dioxide on corrosion at high acidity and the retarding effect at low acidity.

protective covering (see Fig. 26 (a) and (b), showing the corrosion of tin-plate by citric acid in the presence and absence of sulphur dioxide). This is interesting, as it suggests an explanation of the results obtained by American workers on the effect of sulphur sprays on the corrosion of canned fruits. They found that with gooseberries (an acid fruit) there was trouble from hydrogen swells when sulphur was present.

This can be explained on the grounds that the sulphur renders the iron *permanently anodic* to the tin and causes the acceleration of corrosion of iron at high acidity.

At low acidity the film of sulphide on the tin seems slightly less protective, although it still appears to give a good deal of protection ; at

the same time the corrosion of the iron is very much reduced. In fact, at *low acidity*, the effect of the sulphur is to lower the corrosion of both metals *as compared with that which occurs in its absence at the same acidity*. Hence it can be understood

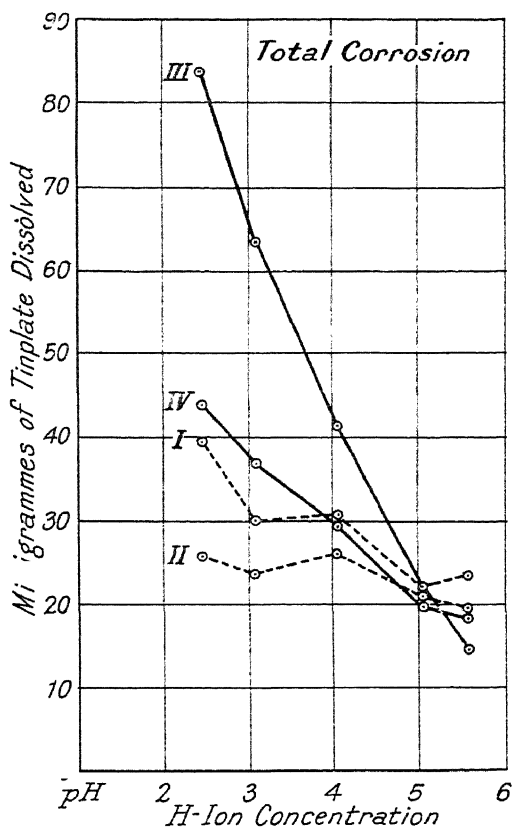


FIG. 26a.—The effect of sulphur dioxide on the corrosion of strips of tin-plate, having equal areas of iron and tin exposed, in buffered solutions containing 5 grams of citric acid per litre, with and without sucrose (*Ann. Rep. F.I.B.*).

that the addition of sulphur compounds (e.g. sodium thio-sulphate) to fruits of low acidity, like cherries, may be beneficial, as was found by Clough, Shostrom and Clark⁸ in America.

Sulphur, as sulphur dioxide or hydrogen sulphide, is likely, therefore, to be harmful at high acidity and beneficial at low acidity, and is effective when present in minute quantities (two parts per million of sulphur dioxide has a noticeable effect; eight parts per million approaches the maximum effect). These quantities are well within the limit of sulphur dioxide allowed in foodstuffs, but at the present stage it is necessary to exercise caution in adding sulphur dioxide to fruits with which it has

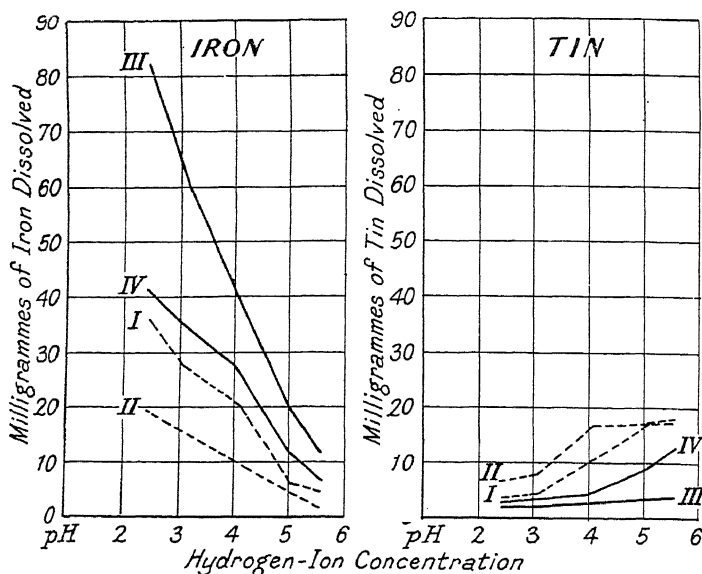


FIG. 26b.—As Fig. 26a, but showing the corrosion of the iron and tin respectively in the same experiment (*Ann. Rep. F.I.B.*).

not been tried. Also it seems doubtful whether it is safe to recommend the method to canners who have no means of keeping chemical control over their products.

The principal considerations relating to the mechanism of corrosion in cans are summarised by Morris and Bryan as follows :—

- (a) The enormous protection afforded to iron by contact with tin as the result of the high over-voltage of hydrogen on the latter.

- (b) The inhibiting effect of traces of tin and certain organic substances on the corrosion of iron.
- (c) The action of sulphur compounds on tin-plate.
- (d) The accelerating effect of oxygen or oxidising agents on corrosion.
- (e) The fact that, although tin alone is not attacked by organic non-oxidising acids in the absence of oxygen, it is attacked by these acids when in contact with iron at a rate depending upon the relative areas of the two metals and the hydrogen-ion concentration of the corroding medium.

The conditions favouring the formation of hydrogen swells and perforations are :—

- (1) Low acidity (syrup in the neighbourhood of p_H 4), unless sulphur is present.
- (2) Lacquer on the inside of the can, although this is a necessity with red fruits in order to lessen discoloration.
- (3) The presence of substances, such as sulphides, which accelerate corrosion of iron with products of high acidity.
- (4) Storage of canned goods at high temperatures, and inefficient cooling of the cans after processing.
- (5) The presence of solids and other substances, which either absorb or combine with tin salts, and so encourage de-tinning and, at the same time, decrease the inhibiting action of tin salts in solution on the corrosion of iron.
- (6) Inefficient exhausting, which leaves oxygen in the can after sealing and encourages de-tinning, and the presence of anthocyanin pigments or other oxidising agents which act as hydrogen acceptors or depolarisers, and also encourage de-tinning and intense local action on the iron.
- (7) Insufficient headspace in the can, so that any hydrogen which may be produced will soon cause swelling.

The remedial measures suggested are :—

- (1) Careful attention to technical and mechanical details, such as efficient exhausting and perfect sealing.
- (2) Cool storage of canned foods.
- (3) Adjustment of the acidity of the syrup in certain cases.
- (4) Care in selecting sugar free from sulphur compounds, and excluding sulphur from other sources when canning fruits of high acidity.
- (5) The use of inhibitors of corrosion, like beet sugar, is also put forward as a possibility, although this has not yet been fully tried out in practice ; and attention is drawn to the possibility of adding sulphur compounds, as suggested by Clough, Shostrom and Clark, for products of low acidity. It is obvious, however, that caution is needed here, owing to the enormous effect on corrosion of varying the H-ion concentration when sulphur is present.

The factors encouraging hydrogen swells and perforations are thus practically the same, but oxidising agents may in some cases cause intense local action without much production of hydrogen, since the latter reacts to some extent with the oxidising agent instead of being liberated as gas. Where this happens a perforation may occur without the formation of a hydrogen swell.

REFERENCES.

- 1 MORRIS, T. N., and BRYAN, J. M., "The Corrosion of the Tin-plate Container by Food Products," Department of Scientific and Industrial Research, Food Investigation Board Special Report No. 40, 1931, price 1s. 6d. (This contains a bibliography of corrosion, to which reference must be made for the work of many of the authors mentioned.)
- 2 EVANS, U. R., "Discussion on the Corrosion of Zinc and Cadmium Coatings," *Trans. Amer. Electrochem. Soc.*, 1930, 58, 35.
- 3 HIRST, F., and ADAM, W. B., "Springers, Hydrogen Swells and Perforations in Canned Fruit," *Canners' Bull.* No. 1, Univ. Bristol Res. Sta., Campden, Glos., England.
Supplement to *Canners' Bull.* No. 1, Univ. Bristol Res. Sta., Campden, Glos., England.

- 4 MRAK, E. M., and RICHERT, P. H., "Hydrogen Swelling of Canned, Ready-to-serve Prunes," *Fruit Products Journal*, 1928, 8, 11, 14 and 17; *ibid.*, June, 1931.
"The Swelling of Canned Prunes," Univ. Cal. Agric. Exp. Sta., Bull. No. 508, 1931.
- 5 KOHMAN, E. F., "Acidity and Corrosion in Canned Fruits," *Journ. Ind. and Eng. Chem.*, 1930, 22, 515.
- 6 CULPEPPER, C. W., and CALDWELL, J. S., "The Behaviour of Anthocyanin Pigments in Canning," *J. Agric. Res.*, 1927, 35, 127.
- 7 LEACH, "Food Inspection and Analysis," John Wiley, N.Y., p. 962.
- 8 CLOUGH, R. W., SHOSTROM, O. E., and CLARK, E. D., "Sulphur, Friend or Foe?" *Canning Age*, 1930, 11, 402.
- 9 Annual Reports of the Food Investigation Board from 1929 to 1931, H.M. Stationery Office. Various statements by T. N. Morris and J. M. Bryan in the section on Canning.

CHAPTER VI.

THE EXAMINATION OF CANNED FRUITS FOR FACTORY CONTROL AND DIAGNOSIS OF THE CAUSES OF SPOILAGE.

POINTS of importance in the examination of canned goods are as follows :—

Syrup strength.

Acidity (total acidity and hydrogen-ion concentration).

Appearance of the can ; condition of seams ; condition of enamel or lacquer ; evidence of corrosion.

Tin content.

Volume of headspace ; volume and composition of the gas in the can ; vacuum in the can at the time of opening ; original vacuum as indicating the efficiency of the exhaust.

Evidence of contamination by micro-organisms.

Syrup Strength.

This is best determined by means of a refractometer provided with a sugar scale, or by a saccharometer of the Brix, Baumé or other type with the aid of Table XIV., p. 92.

Acidity.

The total acidity is determined by titration with N/10 sodium hydroxide, using phenolphthalein as indicator. In the case of highly coloured syrups the titration may either be made electrometrically, using the quinhydrone electrode, or by using as an indicator a piece of phenolphthalein paper, inserted into

the end of an open glass tube, this tube being used as a stirrer during the titration, and withdrawn for inspection after each addition of alkali. The hydrogen-ion concentration is conveniently determined by means of the quinhydrone electrode.

Appearance of the Cans.

An opinion with regard to the extent of de-tinning may be formed by examination of the interior of plain cans. The condition known as "feathering" is normal, and does not necessarily indicate much de-tinning. The latter condition is shown by actual disappearance of the tin coating in patches which may readily be seen. The lacquer on the inside of lacquered cans should also be examined for scratches and for any tendency to peel off.

Leaks in the bottom seams may be tested with a special apparatus, by means of which the open tops of the cans are closed by a pad through which air is forced while the cans are immersed in water. Filled cans suspected of minute leaks may be placed in a chamber under a pressure of about 20 lb. Under these conditions, if small leaks are present, the pressure within the can gradually becomes equal to that outside it, and, when the outside pressure is released, faulty cans will be found to bulge. Cheftel¹ has pointed out that it is not reasonable to seek for very small leaks by exerting a pressure inside the can, since it is possible for such a pressure to cause them to become completely blocked up by organic débris so that they will not be seen. By exerting the pressure from the opposite direction, as in the method just described, and in others favoured by Cheftel, this difficulty is overcome. Cheftel recommends the method of Belser, which he has made more sensitive by means of ultra-violet rays. A circular hole is cut in the bottom of the can, which is emptied and rinsed out with water. The can is then held for an hour in boiling water to cleanse it thoroughly. A brass tube is soldered to the opening, the can half-filled with water, connected to a vacuum-pump and partially exhausted. (It must not be allowed to collapse.) The bottom of the can

is then immersed in a bath containing a 5 per cent. solution of fluorescein heated to 60° or 70° C. After two or three hours the liquid in the can is examined to see whether the dye has passed through the bottom seam. By gradually immersing more and more of the can in the liquid the exact position of any leak may be determined, although care must be taken not to immerse the lid in case there should be a leak where the brass tube was soldered in. Very minute leaks can be detected in this way, since 1 part of fluorescein in 500,000 parts of water is made visible with the aid of a Wood lamp (3630A) when the solution is examined in a tube of non-fluorescent glass.

A biological method, also recommended by Cheftel, for detecting leaks is due to Mormann. The suspected can has a circular hole cut in the bottom as before, and is emptied and rinsed out. It is filled with nutritive bouillon and carefully closed by soldering a disc of tin-plate over the hole. This closure is tested by plunging the can in hot water to see whether air bubbles escape and, if none are observed, the bouillon is sterilised by heating for thirty minutes at 120° C. The can is allowed to cool in a suspension of gas-forming bacteria, and incubated for three days. If swelling occurs, a leak is indicated.

Tin Content.

As the result of many trials, Morris and Bryan recommend the following method of estimating tin, as being rapid and convenient :—

An aliquot portion of the material to be tested is placed in a Kjeldahl flask and heated with 50 c.c. of concentrated nitric acid and 10-15 c.c. of concentrated sulphuric acid. The heating is continued until all brown fumes have been driven off and the volume of liquid in the flask is 10-15 c.c. If the solution is not water-white more nitric acid must be added and the heating continued. The flask and contents are allowed to cool, a small quantity of potassium chlorate is added, together with 15 c.c. of concentrated hydrochloric acid and 10 c.c. of water. The mixture is then heated until white fumes appear and the

solution is clear ; if the solution is cloudy the last process must be repeated, and the volume not reduced quite so far. The clear solution is washed out of the Kjeldahl flask into a conical flask of about 200 c.c. capacity with several small volumes of distilled water, draining carefully between each washing ; 25 c.c. of concentrated hydrochloric acid are added, and about 0.5 gram of aluminium foil cut into small pieces is added to reduce the tin to the stannous condition. During and after the reduction, air is prevented from entering the conical flask by a rubber stopper, fitted with a bent glass tube, leading into a beaker containing 10 per cent. solution of potassium bicarbonate. When evolution of hydrogen has ceased, the flask is cooled by immersion in ice and water, which causes potassium bicarbonate to be drawn into it with evolution of carbon dioxide. The solution is then quickly titrated with N/100 iodine from a burette, using starch as indicator. The burette may be fitted with a rubber stopper below the tap to fit the flask loosely and so reduce the access of air. It is advisable that the quantity of sample taken should be such that about 5 milligrams of tin are present, and blank tests should be carried out on the chemicals used.

Volume of Headspace ; Gas Collection and Analysis ; Vacuum.

If the headspace is almost absent, great strains may be placed on the cans during processing owing to the expansion of the contents. This may sometimes cause the cans to be permanently bulged. An insufficient headspace also allows little room to accommodate any formation of hydrogen as the result of corrosion, hence cans having this fault are liable to become hydrogen-swells very quickly. With a headspace which is too large, there is liable to be a complaint of short weight, also the amount of oxygen left in the can may be sufficient to affect corrosion appreciably, especially if the arrangements for exhausting the cans are not efficient. The

usual filling-line is $\frac{1}{4}$ to $\frac{5}{16}$ inch, which means that after sealing the top of the liquid will be about $\frac{1}{8}$ inch from the lid.

Apparatus for collecting the gas from cans has been described by Baker,² Clough, Shostrom and Clark,³ and Savage.⁴ For testing the vacuum, small gauges with fine capillaries are specially constructed by the American Can Company to pierce the can and register the vacuum direct in inches.

In the case of fruits in syrup a good deal of information may be gained without elaborate apparatus by the following methods :—

- (1) Weigh the can to the nearest gram.
- (2) Immerse the can in clean water, and puncture it at the top, near the edge, with a sharp instrument, while holding an inverted bottle filled with water over the hole to catch the gas as it rises. In the case of hydrogen-swells it will be found advisable to make the hole small at first, and enlarge it after the pressure has been released. By alternately pressing and releasing the top of the can and tilting so that the hole is uppermost, all the gas can be expelled and collected for measurement and analysis.
- (3) Wipe the outside of the can and weigh again. The gain in weight in grams gives the volume of the headspace in c.c.

Gas Analysis.

This may be accomplished in an apparatus either of the Haldane, Orsat or Burrell type. The gas may contain carbon dioxide in small quantity, and a little oxygen. Nitrogen, however, constitutes the main bulk in a sound can, while hydrogen-swells naturally contain a large proportion of hydrogen. Calculations are carried out on the following lines, and are best illustrated by actual examples :—

Ex. 1.—One-lb. Can of Blackberries in Syrup. Appearance normal.

Weight of can and contents	510.0 gm.
„ „, water drawn in as described previously	530.8 gm.
Headspace	20.8 c.c.
Volume of gas collected	14.8 c.c.
Consisting of :—	
Carbon dioxide	1.5 „
Oxygen	0.2 „
Hydrogen	3.4 „
Nitrogen	9.7 „

$$\text{Volume of original air in the can } \frac{9.7 \times 5}{4} = 12.1 \text{ c.c.}$$

∴ Volume of original oxygen = 2.4 c.c.

Oxygen absorbed = original oxygen - residual oxygen = 2.2 c.c.

Original vacuum in inches =

$$30 - 30 \frac{(\text{Volume of original air} + \text{volume of carbon dioxide})^*}{\text{Volume of headspace}}$$

$$= 30 - 30 \frac{(12.1 + 1.5)}{20.8} = 10.4 \text{ in.}$$

In this case the volume of the headspace was normal for the size of can, and the original vacuum in the can shows that the exhaust was moderately efficient.† A few c.c. of hydrogen was produced by corrosion, but not enough to swell the can. The hydrogen required to do this must exceed the difference between the volume of the headspace and the sum of the nitrogen, residual oxygen and carbon dioxide by a few c.c. In this case, it would be

$$20.8 - (9.7 + 0.2 + 1.5) = 9.4 \text{ c.c.}$$

plus an additional 3 or 4 c.c., depending on the flexibility of the can lid.

Ex. 2.—The original vacuum in this case was too small, and points to an insufficient exhaust. (See data on next page.)

The quantity of hydrogen necessary to produce a swell was,

$$29 - (18.6 + 0.7 + 1.1 \text{ c.c.}) = 8.6 \pm \text{approx. } 3 \text{ c.c.}$$

= 11.6 c.c. for a can presenting a surface considerably larger than the preceding one.

* The carbon dioxide is assumed to be present originally in the fruit. There is evidence, however, that some may be formed by oxidation of the acids or sugars present.

† A can which showed 10 to 15 inches on a vacuum gauge would be considered to have been efficiently exhausted.

Two-lb. Can of Greengages. Swollen.

Weight of can and contents	754.0 gm.
„ after puncturing under water and removing gas	783.0
Headspace	29.0 c.c.
Total gas collected	47.6
Consisting of :—	
Carbon dioxide	1.1
Oxygen	0.7
Hydrogen	27.2
Nitrogen	18.6
Original air calculated from the nitrogen	23.2
∴ Original oxygen = 4.6 c.c.	
Oxygen absorbed = 3.9 c.c.	

$$\text{Original vacuum} = 30 - 30 \frac{(23.2 + 1.1)}{29} = 4.9 \text{ in.}$$

Slight solubility errors will be encountered in this method for which it is scarcely possible to make corrections ; also, any air present in the fruit when canned will contain a higher percentage of nitrogen than ordinary atmospheric air, and will therefore give rise to a small error in the calculation of the original air. The method may be regarded, however, as sufficiently accurate for diagnosing the efficiency of the exhaust.

The calculations do not hold good in the case of “breathers,” i.e. cans with very small leaks. Breathing during part of the can’s history may, however, be suspected when an excessive amount of nitrogen is revealed by the gas analysis, i.e. when the volume of original air, calculated from the volume of nitrogen found, exceeds the total headspace.

Gas-analysis Apparatus.

The apparatus for gas analysis employed by the Author was adapted from the Orsat apparatus, and is shown in Fig. 27.

The distinctive features are :—

- (i) All samples of gas are measured as dry gas at N.T.P. by making use of the principle employed in Lunge’s Gas Volumeter. For this purpose the closed and movable graduated “reduction” tube (A)* is con-

* A drop of moisture rests on top of the mercury in (A). (See Lunge and Keane, “Technical Methods of Chemical Analysis,” Vol. I, p. 83 (1924), pub. Gurney & Jackson, London and Edinburgh.)

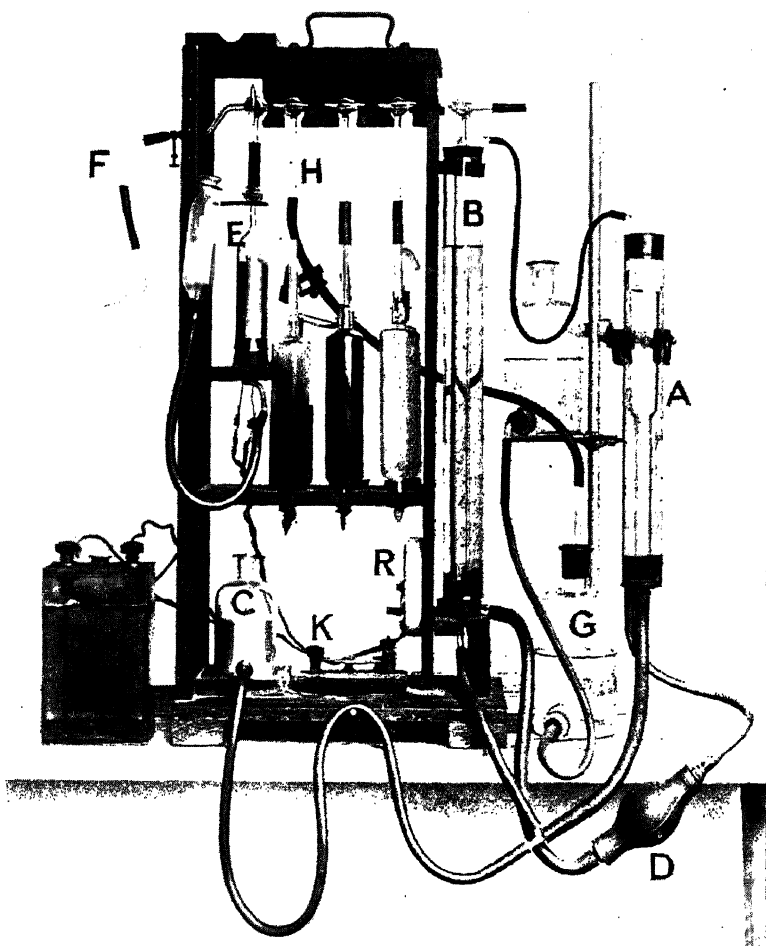


FIG. 27.—Apparatus for gas analysis adapted for making automatic corrections to N.T.P.

- A. "Reduction"-tube.
- B. Measuring-tube.
- C. Levelling-bottle.
- D. Pump for circulating water through the jackets of A and B.
- E. Haldane's explosion-pipette.
- F. Inlet for washing out capillaries.
- G. Aspirator containing nitrogen.
- H. Attachment for third absorption-pipette connected with nitrogen supply.
- K. Tapping-key.
- R. Resistance between explosion-pipette and battery.

[To face page 140.

nected with the gas burette (B) and the levelling bottle (C). (A) and (B) are water-jacketed, and the water can be circulated through both so as to equalise the temperature by means of the pump (D). Readings are taken by releasing (A) from the clamp and holding it against (B) with the right hand. With the left hand (C) is raised or lowered until the level of the mercury in (A) and (B) is the same and the gas in (A) occupies the volume (previously determined) which it would occupy when dry at N.T.P. The volume of gas in (B) which is now also at N.T.P. is then read off.

- (ii) All "dead" capillary spaces are eliminated through the position of the taps.
- (iii) Hydrogen is estimated by explosion with oxygen in a Haldane explosion pipette (E).
- (iv) The whole capillary system is readily washed out with water drawn in through (F).
- (v) All the capillaries can be washed out with nitrogen from the aspirator (G) either through (F) or through the open connection leading to the third absorption pipette (H). (This pipette contains pyrogallol, but is merely used as a buffer to protect the pyrogallol in the second pipette with which it is connected at the back.)

Examination of Raw Materials.

Sulphide or Sulphite Content of Sugar.—This may be estimated rapidly and conveniently by the method outlined by Bryan,⁵ with an apparatus and technique essentially similar to that used for the Gutzeit Test for Arsenic.

The generating bottle is of about 150 c.c. capacity, and is fitted with a waxed cork and a tube (15 cm. by 12 mm.), having a constriction about one-third of the distance from the top to receive a plug of cotton wool. This tube is also provided

with a waxed cork through which passes a tube (15 cm. by 5 mm. bore), constricted 7 cm. from the top to retain the test-paper in position.

The lead acetate test-papers are prepared by soaking filter-paper in a 25 per cent. solution of neutral lead acetate, drying them in air, and then cutting them into strips (6 cm. by 4 mm.); these strips are kept moist by placing them in a desiccator in which the usual dehydrating agent is replaced by wet pumice. After each test the lower tube should be dried and a fresh plug of cotton wool inserted.

In making a test 25 grams of zinc pellets (free from sulphur) are placed in the bottle, and washed with dilute hydrochloric acid, followed by air-free distilled water. The zinc is covered with 50 c.c. of air-free distilled water, and the sugar sample introduced. Fifty c.c. of hydrochloric acid (1 : 1) are added, and the connecting tubes at once placed in position. After a few seconds the bottle is shaken gently, and then allowed to stand for one hour, after which the test-paper is removed, dipped in molten paraffin, and compared with standard stains. The sample taken should be of such a size that the stain falls within the scale of standards given below.

Preparation of the Standard Stains.—Saturate air-free distilled water with sulphur dioxide from a siphon; dilute this solution to a convenient strength with air-free distilled water, and determine the sulphur dioxide present by means of N/20 iodine solution. From this prepare five solutions containing 0.0001, 0.0002, 0.0003, 0.0004, 0.0005 gram of sulphur dioxide, respectively, and 10 grams of pure sucrose per 100 c.c. Air-free distilled water must be used, and every precaution taken to prevent any oxidation of the sulphur dioxide during manipulation. Standard stains corresponding to 0.005, 0.010, 0.015, 0.020, 0.025 mgrm. of sulphur dioxide will be obtained when 5 c.c. of each of the above solutions are used in the apparatus. Since the test is also applicable to the determination of traces of hydrogen sulphide, it is probably advisable to express the stains in terms of sulphur. Attempts were made to differen-

tiate between the sulphur in the two forms, but no satisfactory method was evolved.

It was noticed that more intense standard stains were obtained when sulphur-free sugar was present than from plain sulphur dioxide solutions. Probably the sugar prevents displacement of sulphur dioxide by the hydrogen before reduction has occurred. When standard stains were prepared under these conditions with known amounts of hydrogen sulphide and sulphur dioxide, a comparison showed that one part of hydrogen sulphide was approximately equivalent colorimetrically to two parts of sulphur dioxide, thus indicating that complete reduction of the sulphur dioxide had occurred.

It is necessary to carry out a " blank " test, and it is obvious that the quantity of sugar required in the test will vary according to the amount of sulphur dioxide present. Thus when 1 part per 1,000,000 of sulphur dioxide is present 10 grams of the sugar will be found convenient, whereas when there are 20 parts per 1,000,000 only 1 gram is necessary ; hence a preliminary trial should be carried out to ensure that the stain may fall within the prescribed range of standards.

Tin-plate.—This is sometimes tested either by allowing a solution of gelatin containing hydrochloric acid and potassium ferricyanide to set on the surface of the tin-plate sheet, or, better still, by soaking paper coated with gelatin in an acidified solution of potassium ferricyanide and leaving it in contact with the tin-plate. Blue spots which appear after a short time, or after the paper has dried and peeled off, indicate pin-holes in the tin coating. A method which has also been found useful in testing the covering efficiency of the tin coating is as follows :—

Rings of plate glass about 3 inches internal diameter and $\frac{1}{2}$ inch in thickness are clamped on to the surface of samples of tin-plate of convenient size, in such a way that liquid poured into the space enclosed will not flow under the glass.* Twenty c.c. of standard hydrochloric acid are introduced into this space

* A little thick vaseline prevents this from happening.

by means of a pipette, covered with clock glass, and left for a definite time (say twenty-four hours). At the end of this time, iron is estimated in the acid solution by evaporating to dryness with a little potassium chlorate, igniting, dissolving the ferric oxide in a small quantity of hydrochloric acid, and titrating with a solution of titanium chloride, suitably diluted for estimating very small quantities of iron. If the weight of the sample of tin-plate is known, the weight of tin dissolved can be calculated or, alternatively, the tin in solution can be estimated by titration with iodine as described (p. 136), and the iron found by difference.

The procedure is similar with both lacquered and plain tin-plate, except as regards the strength of the standard hydrochloric acid employed. For lacquered plate, N/1 acid should be used ; for plain, N/10 is strong enough. By using a tin-plate of proved good quality as a standard, inferior plate may be detected by comparative tests.* Further tests may then be carried out in order to ascertain the total weight of tin per base box. For this estimation the method already described for tin can be adapted, but it is unnecessary to add aluminium to bring about reduction of the tin from the stannic to the stannous condition, since this is accomplished by the iron. It is found that a heavy coating of tin may not necessarily be as good as a thinner coating if the latter is more evenly applied.

Contamination by Micro-organisms.

Bacteria do not, as a rule, thrive in media as acid as canned fruits. Contamination with yeasts is, however, occasionally met with either through leaks or under-sterilisation. These cause alcoholic fermentation, and are usually associated with rapid swelling or bursting of the cans. They are readily detected by examining a drop of the syrup under the microscope.

* These tests can also be carried out, several at a time, in the absence of air at constant temperature in a desiccator, exhausted and filled with nitrogen. They have the advantage of eliminating edge corrosion. If preferred, citric acid (1 per cent.) may be used instead of hydrochloric and a longer time allowed.

With certain products, particularly tomato sauces, etc., it is sometimes important to determine how far the fruit was contaminated with moulds, yeasts and bacteria before canning. For this purpose, counts of the dead yeasts, etc., are made by employing a technique similar to that used in making counts of blood corpuscles. The apparatus required consists of a specially made slide and cover glass known as a hæmocytometer. The middle portion of the slide is accurately divided into squares, and ground so that there is a definite depth of liquid between it and the cover glass. With suitable dilutions of the liquid to be examined, it is possible, by counting the spores in a number of squares of definite area, to estimate the number of spores per unit volume, and also to form an opinion on the extent of contamination by the vegetative hyphæ of moulds. In U.S.A. certain standards have been adopted by the Bureau of Chemistry of the Department of Agriculture with regard to the numbers of moulds, yeasts and bacteria which may be permitted in tomato products.^{6, 7, 8}

REFERENCES.

EXAMINATION OF CANNED FOODS.

- 1 CHEFTEL, H., "Les Boîtes Bombées dans l'Industrie des Conservees alimentaires," Bull. No. 1. Etablts. J. J. Carnaud. Forges de Basse Indre. Laboratoire de Recherches Biologiques.
Also "Chimie et Industrie," 1930, 24, 544.
- 2 BAKER, H. A., "Apparatus for Quantitative Extraction of Gases in Canned Food Containers," 8th Int. Cong. Appl. Chem., 1912, 18, 43.
- 3 CLOUGH, R. W., SHOSTROM, O. E., and CLARK, E. D., "A Study of the Gases in Canned Foods," Univ. Washington Publ. Fish., 1925, 1, 86.
- 4 SAVAGE, W. G., "Canned Foods in Relation to Health," 1923, p. 131.
- 5 BRYAN, J. M., "Note on the Sulphide-Stain Method for Determining Small Quantities of Volatile Sulphur in Sugar," *Analyst*, 1928, 53, 589.
- 6 CRUESS, W. V., "Commercial Fruit and Vegetable Products," McGraw-Hill Co., New York, 1924.
- 7 HOWARD, B. J., Bull. No. 581, U.S. Dept. of Agric.
- 8 CRUESS, W. V., and CHRISTIE, A. W., Laboratory Manual of Fruit and Vegetable Products, New York.

CHAPTER VII.

FRUIT BOTTLING.

THE principles involved in bottling fruits are much the same as for canning in metal containers, and the process scarcely demands separate treatment, except in the following respects :—

1. Since the product is visible to the purchaser more attention is often paid to the appearance and quality of the pack than in ordinary canning. The greatest care is therefore exercised in sorting, slicing and arranging the fruit in the bottles. It is also necessary to see that the bottle is quite full of fruit, and that the fruit is covered with syrup. This is brought about by some treatment to shrink and displace air from the fruit before filling. Thus, plums and gooseberries may receive a short blanch in hot water and strawberries may be partially cooked in strong syrup and allowed to stand in the syrup for several hours. Delicate fruits like raspberries and currants cannot, of course, be treated in this way but, if packed reasonably tightly, will fill the bottle.

The proportion of fruit to syrup is greater in bottling than in canning, hence it is usual to use heavier syrup in order to attain the degree of sweetness necessary to make the product palatable. This is seen in comparing Table XVII. with Table XVIII., which give the strengths of syrup used in canning and bottling respectively. The bottles are filled with syrup, so that at the hottest part of the cooking period the syrup practically touches the cap but does not flow out.

2. Problems of corrosion enter very little into fruit bottling, as the fruit-syrup need not come into prolonged contact with the cap of the bottle ; it is wise, however, to take

the precaution of using caps which have been double-lacquered on the inside.

Other problems, such as leakages from the cap and breakages, may be serious. Leakages are overcome by care in the manufacture of the bottles and by the choice of well-fitting caps and rubber gaskets, sufficiently flexible, and of good quality, and it should be remembered, in this connection, that the joint made by a flat gasket on a flat surface is not usually as reliable as when either the gasket or at least one of the surfaces to which it is applied is rounded.

Breakages have been lessened during recent years by improvements in the quality of glass which have rendered it less brittle and less easily cracked than formerly by sudden changes in temperature, but such changes should be made as gradual as possible. There should, therefore, be an even temperature-gradient if a cooker of the conveyor type is used, starting from about 140° F., rising to 200° F. to 210° F., and in some cookers falling again to about 120° F. or 140° F. (depending on the size of bottle and method of handling). The tops of the bottles may be submerged while the temperature is rising, but must be above water before it begins to fall, so that there is no risk of non-sterile water being sucked through the gaskets. With the open-tank type of non-continuous cooker the bottles are covered with cold or warm water, which is steadily raised to boiling-point and can be run off after the cooking period. The bottles are thus mainly air-cooled and, since this is slow, i.e. since cooking continues for a time after the water is run off, the actual period of heating may be correspondingly reduced. If it is desired to hasten cooling, the hot water may be run off to uncover the tops of the bottles and cold water steadily allowed to flow in, with the outlet valve still open, and at such a rate that the caps do not again become covered.

3. Glass is rigid, hence expansion of the contents of a bottle might fracture it unless the escape of gas or superfluous liquid could take place through the cap. Screw caps are therefore left slightly loose and tightened while the bottle is still

hot, and as it is removed from the cooker. Other types of caps are clipped on with strong spring clips which permit the release of internal pressure, but are sufficiently tight to cause the rubber gasket to seize hold of the surface with which it is in contact and prevent air from entering as soon as the bottle begins to cool. When the bottles are quite cold the lids are held in position by atmospheric pressure, and these clips may be removed.

4. In storing red fruits in bottles, it must be remembered that exposure to light accelerates fading of the colour.

Before leaving the subject of bottling fruits, it should be mentioned that recent tendencies are to use ordinary jam jars for this purpose, and to mechanise the process much more than has generally been done. The jam jars are made of a glass which will withstand considerable changes of temperature without cracking, and are either carefully standardised or specially adapted at the necks to accommodate various types of metal caps which seal them hermetically. The jars may be filled with fruit, "syruped" with hot syrup, exhausted by heating in a bath, capped and sealed and finally processed, thus

TABLE XVIII.

STRENGTHS OF SYRUP REQUIRED FOR BOTTLING VARIOUS FRUITS.

Fruit.	Lb. of Sugar per Gallon of Water.	Degrees Brix.
Blackberry . . .	10 to 12	50 to 55
Black currant . . .	15 „ 17	60 „ 64
Damson . . .	15 „ 17	60 „ 64
Plums . . .	8 „ 9	44·4 „ 47·7
Gooseberries . . .	8 „ 9	44·4 „ 47·7
Raspberries . . .	10 „ 12	50 „ 55
Loganberries . . .	17 „ 20	64 „ 66
Sour cherries . . .	9 „ 11	47·7 „ 52·7
Red currant . . .	17 „ 20	63 „ 66
Rhubarb . . .	10 „ 12	50 „ 55
Strawberries . . .	13 „ 15	57 „ 60
Sweet cherries . . .	6 „ 8	37·5 „ 44·5

being treated according to the sequence of processes usual in canning.

Alternatively, if the caps are of a type which permit the air to escape readily during cooking, they may be placed loosely in position after "syruping" and tightened by machine as the bottles come from the cooker.

Certain firms have already developed their own technique for bottling in this way, and an attempt is now being made by Hirst and Adam¹ to develop and standardise a mechanised process for general use.

Bottled fruits should be standardised as far as possible by filling the same weights of fruit and syrup respectively into each bottle. This requires more care than is required in ordinary canning.

REFERENCE.

- 1 HIRST, F., and ADAM, W. B., "Preliminary Report on a Rapid Method of Bottling Fruits," Univ. of Bristol Res. Sta., Campden, Gloucestershire, Miscellaneous Publications No. 1.

PART III.
DRIED FRUITS.

CHAPTER VIII.

DEGREES OF DRYNESS AND ESTIMATION OF
MOISTURE CONTENT.

THE preservation of fruits by drying involves the reduction of their water content to a point at which the concentration of the soluble solids (sugar, acids, salts, etc.) has become so high that the material no longer constitutes a suitable substratum for the growth of moulds, yeasts and bacteria or for the occurrence of enzymic changes in the fruit itself. It has the advantage over other methods of preservation of reducing the bulk and weight of the product, thereby reducing storage and transport charges. The chief drawback with dried fruits is their tendency to deteriorate in storage, especially if not dried sufficiently; if over-dried, on the other hand, considerable losses of sugar may occur, as shown in Table XIX. :—

TABLE XIX. (*after Cruess*).

LOSS OF SUGAR FROM RAISINS SUBJECTED TO VARIOUS TEMPERATURES
FOR VARYING PERIODS OF TIME.

Temperature. °F.	Hours Exposed.	Percentage Loss of Sugar.
140	8	0.6
140	16	0.8
140	32	1.0
167	8	1.3
167	16	1.9
167	32	6.2
185	8	8.7
185	16	12.2
185	32	14.9

The U.S. Department of Agriculture has placed the legal limit for moisture in dried apples at 24 per cent. and the Dried Fruit Association permits 22 per cent. According to Cruess,¹ experiments have shown that most fruits containing not more than 23 per cent. of moisture will keep indefinitely. Un-sulphured fruits containing 24-30 per cent. of moisture are said to become mouldy sooner or later, whilst those with more than 30 per cent. soon ferment unless very heavily sulphured. Nichols, Powers, Gross and Noel² recommend somewhat lower limits for moisture than those given by Cruess. They notice that any protection due to sulphuring and blanching tends to pass away during storage, and that products with low moisture content are not readily attacked by insects. They consider that, on the whole, the losses due to extra shrinkage and a longer drying period are far outweighed by the advantages of having a low moisture content. According to these writers dried fruits, high in sugar, should not contain more than 15-20 per cent. of moisture, whilst other fruits and vegetables should not contain more than 5-10 per cent.

The effect of humidity in the storage of dried apples has recently been carefully investigated by Culpepper and Caldwell,³ who recognised that the differences in the quantities of residual moisture considered safe by different workers are mainly attributable to differences in the climatic conditions under which the experimental work was done. They emphasise the fact that the humidity of the storage chamber as well as the initial moisture-content of the material are factors of outstanding importance in the control of deterioration of dried fruits in storage.

In their experiments with dried apples, stored in atmospheres with humidities ranging from complete saturation to complete dryness, Culpepper and Caldwell found that the material either absorbed or gave up moisture until a new moisture-content in equilibrium with the moisture of the atmosphere in the chamber had been reached.

At relative humidities of 18.8 per cent. or less, the dried

material retained its original colour, flavour and odour unchanged for three years. At relative humidities between 47 and 80.5 per cent., growth of moulds and yeasts did not occur, but the fruit gradually became brown, rancid and unpalatable. The rapidity of these changes increased with increase in humidity throughout a series of experiments. They occurred with dried fruit which originally contained only 9 or 10 per cent. of moisture and were not prevented by treatment with sulphur or salt or by heating to 80° C. prior to drying. At relative humidities higher than 80.5 per cent. the absorption of water was sufficient to permit rapid and abundant development of moulds and yeasts which destroyed the material within a few months. Of the various treatments to which the fruit had been subjected before drying, that with sulphur dioxide retarded the development of these changes somewhat longer than the others. Sodium chloride was next in effectiveness, but its reaction with some constituent of the apple produced a greyish-white colour in some varieties. Of the different varieties of apples tested, deterioration was most rapid in one which combined the highest acidity and astringency with lowest content of sugar.

Culpepper and Caldwell found evaporated apples to be highly hygroscopic. Material containing 13-15 per cent. of moisture was in approximate equilibrium with the atmosphere over sulphuric acid of 1.30 specific gravity. Fruit with the standard moisture content of 24 per cent. was in approximate equilibrium with air of 75 per cent. humidity at 30° C., and absorbed moisture rapidly when the atmospheric moisture rose above this value. These workers have called attention to the important fact, mentioned in the opening paragraph of this section, that thorough drying means the reduction of moisture, not merely to a point at which mould-growth cannot occur, but to a lower point at which oxidations and other changes not dependent upon the growth of organisms are arrested. They recognise the importance of temperature as a factor in determining the rate of deterioration, but have confined their experiments to temperatures ranging between 20° and 30° C.

The principles outlined by Culpepper and Caldwell in their work on apples apply equally to fruits and vegetables for which the equilibrium values have not yet been established. These authors have pointed out that control of humidity in store-rooms implies the maintenance of atmospheric humidity at, or below, the point of equilibrium with the material stored, and that careful packing involves the use of the most efficient means of preventing the access of atmospheric oxygen.

Analytical Methods for Dried Fruits.

Methods for Determining the Moisture Content of Dried Fruits. [From Nichols, Powers, Gross and Noel.]

The Association of Official Agricultural Chemists has published methods for the determination of moisture in apples by heating in a water-oven, and in other dried fruits by heating *in vacuo*.

In using either method care must be taken to select a thoroughly representative sample of the material. The sample is ground as finely as possible and kept in a sealed jar or tin until ready for use. The directions given are as follows :—

Water-oven Method.

Break up all large lumps of the sample, and weigh 5-10 grams into a metal dish of about 8.5 cm. diameter and provided with a cover. Place the dish on the shelf (not the bottom) of a water-jacketed oven, with suitable vent holes at the top. Dry for four hours * at a temperature not lower than 96° C. Replace the cover, cool in a desiccator, weigh and calculate percentage loss of water.

This method, although it is not claimed to be accurate for other fruits than apples, gives useful comparative results with all kinds of products for factory-control purposes.

* Dried peaches require four and a half hours, apricots three and a half hours and pears five hours.

Vacuum-oven Method.

Prepare the sample, weigh in the metal dish as before, placing the dish in direct contact with the shelf of a vacuum-oven kept at 70°C. for twelve hours at a pressure not exceeding 100 millimetres of mercury. During the drying admit to the oven a slow current of air (about 2 bubbles per second), dried by bubbling through sulphuric acid. With raisins and other fruit, rich in sugar, use about 5 grams of the sample and about 2 grams of finely divided asbestos dried with the dish. Moisten with hot water, mix the sample and asbestos thoroughly, evaporate on the water-bath nearly to dryness, and complete drying in the vacuum-oven.

The above methods for the determination of moisture may be satisfactory for obtaining comparative results with samples of material of the same kind, but are not favoured by

Anderssen,⁴ who points out that a continuous loss of weight, even of apples, has been demonstrated by Archbold⁵ at 50°C.

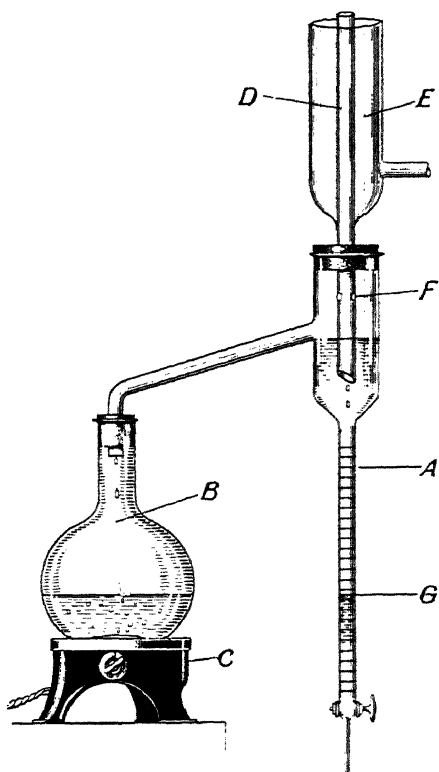


FIG. 28.—Apparatus for the determination of moisture in dried fruits by the toluene-distillation method (after Anderssen).

- A. Burette graduated to 0.1 c.c.
- B. Boiling-flask containing sample and toluene.
- C. Electric hot-plate.
- D-E. Condenser.
- F. Small holes to allow water and toluene vapour to pass into condenser.
- G. Surface between water below and toluene above.

in vacuo, owing to the decomposition of sugar. Anderssen, therefore, recommends the toluene-distillation method of Wiegand and Bullis,⁶ the apparatus for which is shown in Fig. 28. This needs little description beyond that given with the figure. The percentage of moisture in the fruit can be read directly in the graduated burette when the distillation is complete.

Determination of Sulphur Dioxide:

For the accurate determination of sulphur dioxide in dried fruits it is advisable to use the method of Monier-Williams,⁷ which consists essentially in distilling the sample in a current of carbon dioxide through a reflux condenser into pure neutral hydrogen peroxide, the sulphuric acid formed being titrated with standard alkali. It is claimed that this method is an improvement on the method of Wartha,⁸ in which the sulphur dioxide is absorbed by standard iodine and estimated by titration with standard thiosulphate, because volatile sulphur compounds other than sulphur dioxide are not oxidised to sulphuric acid by hydrogen peroxide in the cold, and are therefore not included in the determination. For rapid tests, Anderssen found the method of Wartha the more convenient, and applied a correction for the volatile sulphur compounds initially present in dried fruit not sulphured.

The fruit was thoroughly macerated in a mincing machine, an aliquot part weighed out and put into a boiling flask; 400 c.c. of dilute hydrogen chloride (1 part concentrated hydrogen chloride to 11 parts of freshly distilled water), and 1-2 grams of sodium bicarbonate were then added. The flask was immediately connected to a distillation trap, attached to a condenser, of which the free end was dipping into a 0.1 N iodine solution in an Erlenmeyer flask. The contents of the boiling flask were then boiled for an hour or until 200 c.c. of water had distilled over. The standard iodine solution was surrounded with water and ice to prevent volatilisation of iodine. Blank experi-

ments with the chemicals, according to Anderssen, did not exceed 0.2 to 0.3 c.c. of 0.1 N iodine, and this was added to the blanks obtained with unsulphured fruits. Such a method would be useful for practical control in sulphuring fruits where unsulphured material could be obtained for the blanks, but would be of little use where such material was not available.

Sugars and acids, may be estimated by similar methods to those used in jam and canning control (pp. 73, 134).

CHAPTER IX.

METHODS OF DRYING FRUITS.

THERE are two methods of drying fruits commercially, viz. (a) sun-drying and (b) artificial-drying, by means of heat from a furnace in specially constructed dryers.

Sun-drying can only be practised in tropical or semi-tropical climates, the chief centres being the Mediterranean countries, particularly Asia Minor, Greece and Egypt in the Old World, and California in the New. Under ideal conditions this is the cheapest method of drying.

Artificial-drying, or *dehydration*,* as it is often called, to distinguish it from the older method, has developed most in the more temperate regions of the United States, but it appears to offer certain advantages even in parts of California, where showers of rain during the drying season may cause considerable damage, and involve the extra labour of hurriedly stacking and unstacking the trays on which the fruit is spread. It is claimed by Cruess that the quality (although, possibly, not the appearance) of dehydrated fruit is always better than that of sun-dried for cooking purposes, since the greater rapidity of the process gives less time for the occurrence of enzymic or other changes likely to injure the fruit. There is also less loss in weight from respiration in the early stages.

The greater rapidity of the artificial process also shortens

* This term is used especially in connection with forced-draught driers ; the term " evaporation " is sometimes applied to the older types of driers and to vacuum driers.

the drying season so that fruit-picking may be postponed until the fruit is thoroughly ripe. This affects the sugar content and, consequently, the final yield as may be seen in Table XX. by Bioletti ⁹ for the relation between ripeness and yield in Muscat grapes.

TABLE XX. (after Bioletti,⁹ quoted from Cruess ¹).

THE EFFECT OF MATURITY ON THE YIELD OF DRIED FRUIT FROM MUSCAT GRAPES.

Degrees Balling of Juice at Time of Picking.	Pounds of Raisins per Acre.
18	1786
19	1893
20	2000
21	2107
22	2214
23	2321
24	2428
25	2535
26	2642
27	2749
28	2846

For sun-drying in California it is usual, according to Cruess, to start harvesting when the juice has reached 20°-21° Balling. When the fruit is artificially dehydrated, harvesting can be postponed until about 24° Balling is reached. It is obvious, however, that a statement of this kind will depend a good deal on the scale of production.

The effect of maturity on yield applies to fruits other than grapes, and it is usual to speak of the ratio of the weight of fresh to the weight of dried fruit produced from it as the *drying ratio*. Cruess states that the following are typical drying ratios for various fruits in California:—

Grapes
Prunes	2.4 : 1
Apricots	5 : 1
Peaches	5 : 1
Apples	7 : 1
Most other fruits	5 : 1 or 6 : 1

Treatment before Drying.

A point of difference between sun-dried and dehydrated products lies in the fact that the former acquire the colour of the fully ripe fruit ; the latter retain more or less their original colour, i.e. immature fruit remains pale or green. Whether the fruit is sun-dried or dehydrated, however, its harvesting and treatment before drying present many similar features, and in these respects the two methods may be considered together.

In general, fruit is gathered in riper condition for drying than for canning, but apart from the additional operations of dipping,* sulphuring and traying before drying, the preparation of the fruit is very similar, and much of the machinery and equipment is common to both processes.

Lye Dipping.

See under the individual fruits, especially under " Grapes " (p. 177).

Traying.

For both sun-drying and dehydrating in U.S.A., the fruit is spread on wooden trays with bottoms either of hardwood slat, oiled to prevent the fruit from sticking to them, or of galvanised wire for fruit which does not need to be sulphured. In sun-drying these are often large (8 feet \times 3 feet), and near the end of the process they are stacked and " staggered " in such a way that air can pass between them. For transport purposes they are loaded on trolleys. In dehydrating, the trays are usually smaller (6 feet \times 3 feet or 3 feet square), and are loaded on special trolleys often running on rails. The loaded trolleys are so constructed that little free space is left between them and the walls of the dryer, and the trays are supported on a framework, one above another, so that there is a space of about 2 inches for air to pass between them.

* Dipping is practised for some fruits before canning but is not so general as in drying.

Sulphuring.

Light-coloured fruits are exposed to the fumes of burning sulphur in order to prevent or delay discoloration during and after drying, and to facilitate drying by destroying the capacity of the cell-membranes to limit the passage of water through them. There is also evidence (p. 227) that the presence of sulphur dioxide prevents the destruction of vitamins through oxidation.

According to Nichols and co-workers, sulphuring should be as light as possible, consistent with accomplishing the desired end, and should leave no unpleasant flavour of sulphur in the fruit. It is generally recognised that dehydrated fruits require less prolonged sulphuring than sun-dried, and one of the problems with certain sun-dried fruits is to keep the sulphur content below the limits fixed by law in the various countries, although, according to Nichols and co-workers, such difficulties are rarely encountered with dehydrated fruits.

The usual method of sulphuring in U.S.A. is to place the freshly prepared fruit in a closed chamber of non-porous material (concrete, brick or wood) capable of holding several trucks loaded with trays, "staggered" to facilitate the process, and provided with an entrance for sulphur fumes and an exit for draught. In some cases the sulphur is burnt in a shallow pit or depression in the floor at the back. Another type of apparatus used, particularly for apples, is an elongated box through which the fruit is carried on a wooden slat conveyor. The fumes are conducted into the box from outside, and the speed of the conveyor can be regulated according to requirements.

In South Africa and Australia systematic researches have been carried out on the sulphuring of fruits for drying, in order to render the process less haphazard and to bring the finished product into line with the food regulations of the various countries to which the dried fruit is exported. These regulations are as follows :—

TABLE XXI.

Country or State.	Parts per Million of Sulphur Dioxide.
Great Britain	2000 (750 for raisins)
Canada	2500
Switzerland	2000
Germany, Austria, Hungary	1250
Czecho-Slovakia	1250 (raisins only)
France	1000
Japan	1000 (apricots). None allowed in other fruits
U.S.A. :	
New York State	2000
New Hampshire	None

In experiments in South Africa, Anderssen ⁴ placed the fruit (apricots) to be sulphured on trays in iron tanks painted inside with acid-resisting paint and capable of being tightly closed. Measured quantities of pure sulphur dioxide were introduced from cylinders, and the gas was kept evenly distributed by means of electric fans placed in the tanks. Four concentrations of the gas were employed, viz. 2-3, 4-5, 9-11 and 13-16 per cent., and for each concentration different batches of fruit were exposed for one, two, three and four hours respectively. Each batch of fruit was spread on four trays, one of which was dried entirely in the sun, the others being shaded for varying lengths of time. No definite conclusions were given in this work as regards the best concentration of sulphur dioxide or the period of exposure which, on the whole, gave most satisfactory results, but it was stated that there was no difficulty in obtaining a product of excellent quality in which the amount of sulphur dioxide present was well below 2000 parts per million and even below the French requirement of 1000 parts per million. It was further found that the quantity of sulphur dioxide in the finished product decreased progressively according to the period of shade-drying, and that spraying the fruit with water before sulphuring offered no advantage as regards quality, but, on the other hand, caused more sulphur dioxide to be retained in the finished

product.* It was also shown that little or no oxidation of the sulphur dioxide to sulphate occurred during drying, but further confirmation of this would seem to be required in view of the observation of Nichols and Christie¹⁰ that the *total* sulphur in apples increases progressively if the sulphuring period is prolonged, although the actual content as sulphur dioxide may not reach more than 200-250 parts per million.

With sultanas, owing to the fact that no cut surface is exposed, no satisfactory method was found of reducing the sulphur content below the legal limit. Shade-drying decreased it considerably but not sufficiently. Dipping in water and re-drying in the shade, thrice repeated, was shown by Skibbe²³ to reduce the sulphur dioxide content from 1210 parts per million to 700 parts per million. This would, however, involve considerable extra labour, and Anderssen is of the opinion that it may be necessary to abandon the sulphuring process for this fruit in South Africa and adopt the dipping methods in vogue in California and Australia.

In Australia, methods of sulphuring fruits, particularly apricots,¹¹ have been developed and standardised as the result of the work of Lyon and others, and a report has been drawn up by a committee of experts, the object of which was to recommend a procedure suitable for use in Australia and likely to produce a satisfactory product containing less than 14 grains of sulphur dioxide per pound (2000 parts per million).

The chief recommendations in the report are concerned with the following points :—

1. All fruits should be picked "eating ripe," and any over-ripe or unripe fruit should either be discarded or sulphured separately. This ensures uniform sulphuring, since firm fruit

* Nichols and Christie¹⁰ found, as the result of numerous experiments, that sprinkling with cold water before sulphuring actually decreased absorption, thus contradicting this statement and rendering further investigation necessary. Treatment with hot lye increased the absorption of sulphur dioxide.

absorbs less sulphur than ripe fruit and generally gives an unsatisfactory product.

2. The sulphuring chamber should be sufficiently airtight to extinguish the sulphur fire when all vents are closed and of light material ("Malthoid" was recommended). In the case of movable hoods, precautions should be taken to prevent ingress of air at the base of the hood as, for example, by packing with moist earth. A number of small units is recommended in preference to one large one, so that fruit need not be held for any length of time after cutting and before sulphuring. Thus, when using trays 6 feet \times 3 feet, the size of the chamber should be sufficient to accommodate a stand of about fifteen trays, with a clearance of 6 inches between the trays and the sides and top of the chamber. In stacking the trays in the chamber they should be "staggered" 6 inches to enable the fumes to reach the fruit.

A vent hole 1 inch in diameter should be provided in the roof of the chamber close to the wall farthest from the sulphur fire, when one fire is used, or in the centre of the roof when a fire is placed at each end of the chamber. A movable glass slide for inspection is also recommended.

3. Six to 8 lb. of sulphur (dry) per ton of fresh fruit is recommended. The sulphur pit should be situated just outside at one or both ends of the chamber, with a free entrance for fumes and a small inlet vent to admit the air necessary for combustion. The sulphur should burn steadily all the time the fruit is in the chamber and slight fumes should be apparent at the vent hole. If all the sulphur be burnt before the expiration of the correct period, an excessive draught is indicated which should be reduced in subsequent operations until just a little sulphur is left.

4. Fruit should not stand more than one or two hours between cutting and sulphuring, and it should be stacked from the bottom upwards in the order in which it is cut. It has been shown that fruit absorbs sulphur most rapidly when freshly cut. The arrangement in stacking therefore tends to

bring about uniformity, since the fruit with the driest cut surfaces comes in contact with the most dense sulphur fumes.

5. Four to six hours' exposure is recommended under average summer-day temperatures in Australia. On very hot days four hours is sufficient. It is not thought advisable that fruit should be left in the chamber all night.

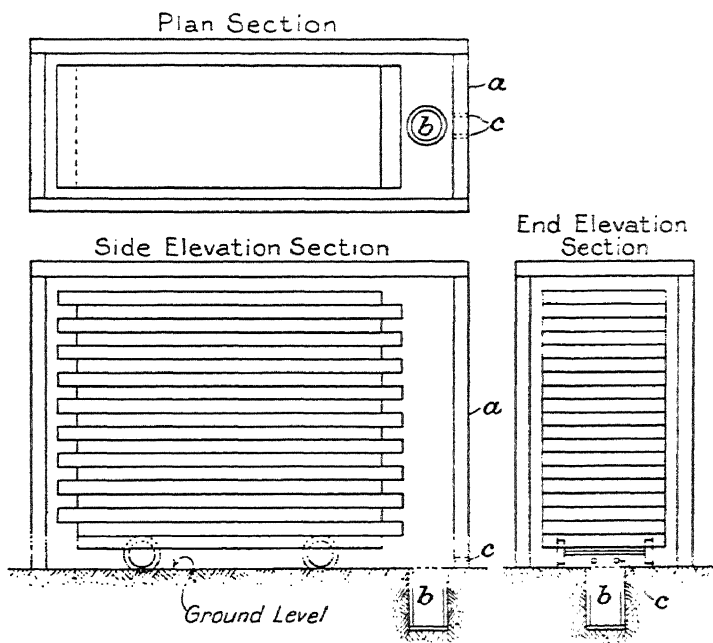


FIG. 29.—Diagram of a simple sulphur house (after Nichols and Christie).
(a) door; (b) sulphur pit; (c) draft holes.

6. The characteristics of correctly sulphured apricots are described as follows: The skin should be easy to detach, the colour should be even, and there should be a distinct exudation of juice into the cups, although the filling of the cups with juice is not a reliable indication of the completion of sulphuring.

Nichols and Christie¹⁰ found that different fruits absorb different amounts of sulphur dioxide, for instance, peaches and apricots take up and retain much more than apples and pears.

They favour permanent sulphuring houses of substantial materials like concrete or brick (see Figs. 29 and 30), and recommend two hours' sulphuring for apricots and three hours for peaches. They state that the final content of sulphur dioxide in dried apricots and peaches should be 1500 parts per million.

The loss of sulphur dioxide from the fruit under different conditions of storage is illustrated by an experiment carried out by Nichols and Christie with dried apples containing, initially, 145 parts per million of sulphur dioxide. Half of these were

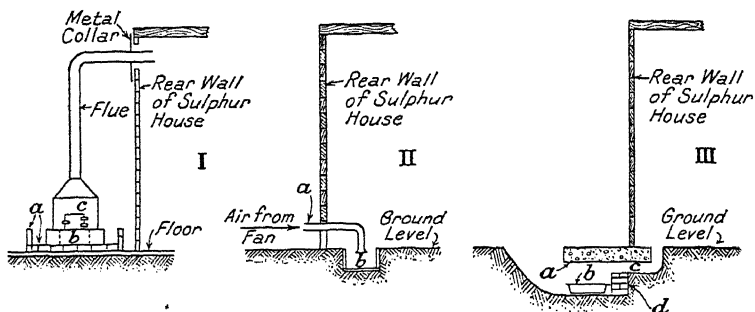


FIG. 30.—Successful types of sulphur burners (*after Nichols and Christie*).

- I. Stove outside sulphur house; (a) safety pan of metal or brick; (b) sulphur pot; (c) metal stove.
- II. Sulphur pit inside house with forced draft; (a) pipe from fan; (b) sulphur pit.
- III. Sulphur pit outside house; (a) tile or concrete pit support; (b) sulphur pan; (c) tile or metal flue pipe; (d) supporting bricks.

packed and stored at Berkeley, California, the other half were packed and sent to New York and back through the Panama Canal. After five months the former contained 68 parts per million of sulphur dioxide and were in good condition, the latter contained only 31 parts per million and had darkened badly. This darkening was mainly ascribed to the loss of sulphur dioxide, and, taking into consideration also the effect of sulphur in preserving vitamins, Nichols and Christie consider that it may ultimately be thought necessary to insist on a certain minimum of sulphur dioxide which the fruit *must* contain rather than a maximum which must not be exceeded.

Details for Drying Various Fruits.

Since each fruit requires special treatment, it is best to consider each of the more important ones separately.

Apples.

Apples for drying should be in firm condition, ripe but not over-ripe, and should give a clean, white product. They are peeled, cored and trimmed mechanically as in canning, and may be cut into slices, rings or dice. To prevent browning they may be given a short preliminary sulphuring, before slicing, in an apparatus of the conveyor type, or the slices may be covered with a 2 per cent. brine as in canning, although Culpepper and Caldwell have shown that this imparts a greyish colour to the dried product with some varieties.

Cruess states that complete sulphuring of apples in the unsliced, peeled condition requires forty-five to ninety minutes, as against twenty to thirty minutes after slicing, or fifteen minutes if the slices are previously dipped in a 3-5 per cent. salt solution. More recently, however, Nichols and Christie have stated that sliced apples should never receive less than one hour's sulphuring—preferably two hours—and that there is no danger of the presence of excess of sulphur dioxide in the finished product: in fact, the difficulty is rather to cause the fruit to take up sufficient for preservation (not less than 200 parts per million).

Apples are dried in almost all the types of dryers in use, from the kiln driers similar to those used for hops to the modern air-blast dehydrators. In stack dryers ten to twelve hours are required for drying, but Cruess states that apples lend themselves well to the parallel or concurrent system (see p. 197), by which it is possible to dry them in two to three hours. The temperatures in use are 180° F. for the lowermost trays in stack driers, and 140°-175° F. for air-blast driers. Nichols and Christie strongly recommend the modern air-blast type of dehydrator for apples and state that, with the counter-

current system, the maximum safe temperature is 160°-165° F., and that for rapid drying the relative humidity should not exceed 18-20 per cent. at the hot end.

Apricots.

Dried apricots have the finest flavour when prepared from fully ripe fruit, but such fruit is difficult to handle and may lose its shape in drying. Under-ripe fruit, on the other hand, yields a shrivelled, tough, product of poor flavour. The fruit should be ripe enough for eating, and slightly riper than is required for canning.

Apricots are never peeled, but are cut in halves around the suture by hand and the stones removed. The halves are arranged, cups upward, in trays and sulphured for two to four * hours, provided that the sulphuring house is warm and airtight except for the minimum necessary draught; the finished product should contain 1500 parts per million of sulphur dioxide.

When the fruit is half- to two-thirds dry in the sun, the trays are stacked, so that the prevailing wind can blow through the stacks, and allowed to finish slowly. According to Cruess, the finished product should contain about 18 per cent. of moisture (Anderssen states that 25 per cent. of moisture is safe, but this would depend upon the conditions of storage, see p. 154). In dehydrating, Cruess recommends that the temperature at the end should not exceed 160° F., and states that 150° F., or below, gives the best results. According to Nichols and Christie, the most desirable humidities at the hot end of the tunnel should be approximately 25 per cent. for apricots, 30 per cent. for peaches, and 35-40 per cent. for pears. The air velocity should be the maximum consistent with efficiency—not less than 500 and not more than 800 feet per minute. At the same time, Nichols and Christie state that dehydrated

* See p. 165, where apricots have been largely used to illustrate the sulphuring process in general. The Australian authorities recommend four to six hours.

apricots never have as good an appearance as sun-dried. Various devices, such as starting in the sun and finishing in the dehydrator, have been tried with more or less success, but it is apparently always difficult to find a market for the dehydrated article. This statement also applies to peaches and pears.

Peaches.

Peaches for drying should preferably be of the free stone type, of large size and high sugar content. They should be firm but ripe, fully coloured and free from soft spots. The fruit is peeled by means of lye (see p. 82) or by hand, or may be left unpeeled. It is halved and stoned as in preparing apricots, and sulphured on trays with the cups upwards for three hours (Nichols and Christie), under the same conditions as apricots. The finished product should contain 1500 parts per million of sulphur dioxide. In artificial drying of peaches the temperature, according to Cruess, should not exceed 145° F., owing to their tendency to caramelize. The relative humidity of the dryer should be about 30 per cent. during the final stages to prevent case-hardening, and the product should be firm, pliable and of a golden-yellow colour.

Pears.

Pears are harvested while still too green for eating and are ready for drying when they begin to turn yellow in storage. The fruit, which may be peeled either by hand or lye or left unpeeled, is cut in halves. Sometimes only the calyx and stalk is removed, sometimes the fruit is cored.

Cruess mentions eight to twenty-four hours as the sulphuring period for cull pears intended for sun-drying in Sacramento, and even forty-eight to seventy-two hours in certain other localities. He states that a pear properly sulphured for sun-drying is soft throughout, since prolonged sulphuring softens the tissues and renders the product light coloured and translucent, a condition said to be favoured in the

trade. These wide variations in the length of the sulphuring period are due to the fact that pears, like apples, do not readily absorb the sulphur fumes. Nichols and Christie give six hours as the minimum sulphuring period when the sulphur is burned by natural draught. Nichols, Powers, Gross and Noel recommend dipping in cold water or weak saline, as for apples, to prevent browning between operations.

For sun-drying, the pears are spread on trays in the sun for one-half to two days, according to climatic conditions, and are then stacked under long sheds so that air can circulate freely between them. Drying under these conditions takes three to six weeks, and the appearance is said to be improved by the slowness of the process. Quicker drying results in a darker and less translucent product.

Prunes.

Prunes are one of the most important of the dried fruits. They are allowed to ripen on the trees until they fall to the ground, either naturally or with very light shaking. Further treatment consists in washing with cold water and dipping in a weak, boiling solution of lye (average strength about 0.5 per cent.) for about fifteen seconds, or until the skins become "checked" (covered with tiny cracks over the whole surface) and the waxy bloom is removed. Some varieties require more careful treatment than others and, in any case, immersion must not be long enough either to cause the skin to come off or to cook the fruit appreciably. After this treatment the fruit is rinsed and spread on trays to dry without any sulphur treatment. In sun-drying, the fruit should be turned occasionally and stacked when about two-thirds to three-quarters dry, so that air can pass freely over it. The dried fruit, according to Cruess, should contain 12-18 per cent. of moisture. It is stated that when properly dried the stone should not slip between the fingers when the prune is pressed, the flesh should be firm and the skin tough.

In dehydrating, the initial temperature must not be too high, as this will cause dripping. The temperatures recommended by Cruess are 110°-130° F. at the start, and 160°-165° F. at the finish, with a relative humidity of at least 20 per cent. to prevent case-hardening.

Whilst the aim in drying prunes in U.S.A. has been largely towards efficiency in mass production, in France (the Agen district) it has been entirely towards quality, expenditure of fuel and labour being regarded as secondary considerations, and it is admitted in many quarters that the French product is unequalled. The French prune is not merely dried, but is, to some extent, cooked in a moist atmosphere, with the result that the flavour is distinctive and in no way resembles that of the raw product. Since there should be room both for the high-quality as well as for the mass-produced product, it is well to give some account of the French process, as recorded by de Castella¹² from a study of French literature on the subject.

French prunes are always dried by artificial heat, and are never dipped or sulphured before drying. The best are of large size, the crop being thinned if necessary with a view to the production of large fruit. According to de Castella, a good prune has a thin black or purplish-brown, coarsely wrinkled skin, either smooth and glossy or velvety and slightly moist to the touch, but *not* wet and sticky. The pulp should be abundant, soft, pliable, but not hard and leathery; it should separate readily from the pit and be of a rich brown colour (in most American types it is amber-yellow); it is mucilaginous, sweetly acidulous, and with characteristic flavour. Compared with these prunes, those dried in the sun have a dull, harsh surface unless finished with glycerine or syrup.

The ovens or *étuves* (see Fig. 31) used in France for drying are of relatively small size. They are constructed of masonry or brick, with hollow walls, provided with diagonal flues, and are, typically, about 7 feet high, 8-9 feet from front to back, and 5 feet 3 inches wide. The firebox, either of wrought or

cast iron, is beneath the front part of the oven, and the fuel is usually wood. Large growers prefer a number of ovens of this size to one of larger capacity. The prunes are spread on trays with bottoms of wire or laths, and are loaded on trucks in five to ten tiers or shelves, each tier holding three to eight trays. The trucks with a charge of $5\frac{1}{2}$ -11 cwt. of fresh prunes are pushed into the oven on rails.

Evenness of heating is essential, and for this purpose the shelves of the trucks are placed wider apart at mid-height

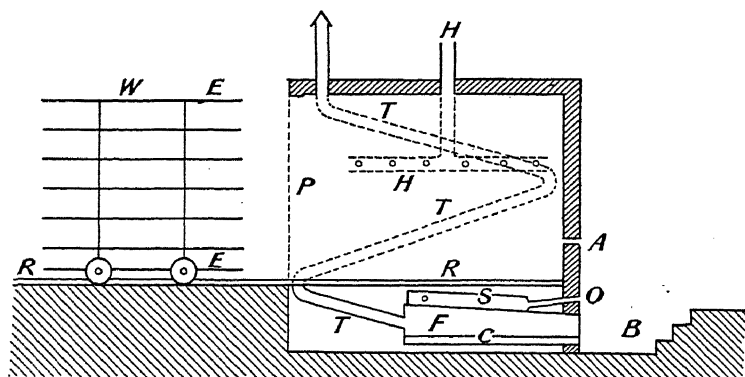


FIG. 31.—Diagrammatic section of prune oven (*from de Castella, after Rabate*).

B, recess for fireman; A, cold air entrance; O, entrance for air to be heated; S, heating chamber; F, fire-box; C, ash-pan; T, T, T, smoke flues; H, H, pipes for removal of moist air; P, door; R, R, rails; W, truck; E, E, shelves for carrying drying trays. (Scale about 6 feet to 1 inch.)

than at the top and bottom, and provision is made for the entry of fresh air and for evacuation of moist air. The air inlets are carefully constructed so that the incoming air can be regulated and distributed evenly. The exit of moist air can also be checked, so that for part of the time the prunes are heated in an atmosphere of steam. The ovens are provided with a thermometer, and the humidity can be judged by the deposition of moisture on a plate of glass in the door.

The general procedure depends largely upon the construction of the oven, different ovens being adapted for slightly

different systems, but in all cases the process is discontinuous, the fruit being drawn out to cool thoroughly at least twice.

The *first heating* period is known as wilting. For this the chamber is usually made very hot, the temperature being brought down by the introduction of the charge of fruit. It usually occupies four to six hours at 113° - 140° F., after which the truck is drawn out to cool.

The *second heating*, or "seconding," occupies four to six hours at 140° - 167° F., after which the fruit is again cooled.

The *third heating*, or "finishing," also occupies four to six hours at 158° - 167° F., and during this period the exit vents are closed for an hour or so about half-way through the process or earlier to promote high humidity. When finished, the fruit is cooled as rapidly as possible. The whole operation, including the cooling periods, occupies from nineteen to twenty-seven hours. Two of the best types of ovens, the Boudie and the Pejac, may be taken to illustrate the details of the process.

Drying with Boudie's Oven.

Two main principles are observed, viz. :—

- (1) The temperature is not allowed to fall when once equilibrium has been established in a given heating period.
- (2) Moisture is not allowed to remain on the observation glass. As soon as any condensation is observed the vents are opened.

For the first heating the empty oven is heated to 212° F., with all vents closed. The load consists of 610 lb. of prunes, and the temperature after the first hour should be 140° F. After an hour the air vents are gradually opened, and after two hours the door is opened slightly to see that swelling of the fruit is not excessive, and, if dripping seems likely to occur, the truck is wheeled out for five minutes. It is then wheeled in again, the thermometer falling to about 129° F. and left for six hours at a temperature not exceeding 131° F. It is then drawn out to cool for an hour.

For the second heating the empty oven is raised to 176° - 194° F., and the truck wheeled in. The vents are opened to let abundant steam out, and the fruit remains for six hours at 140° - 149° F., rising to 158° F. during the sixth hour. The fruit should attain a good brown colour near the end of this process; if this is not the case the temperature should be raised a little. At the end of this period the fruit is again cooled for an hour.

For the finishing process, whilst the truck is outside, the air vents are closed and the temperature of the oven raised to 212° F. The truck is wheeled in and the temperature falls to 140° F. The exit vents are kept closed for about an hour until the glass indicates slight condensation; they are then opened to let out steam. Heating is continued for six hours, gradually reaching 167° F. towards the fifth hour. The air vents are kept open during the later stages to prevent softening of the prunes, and towards the sixth hour the door is slightly opened and the fruit is sometimes left in the oven for an extra hour to dry completely.

Pejac's Oven.

A brief account of the working of this oven, as given by de Castella, illustrates the kind of variation which occurs with different installations.

For the first heating, 8 cwt. of fresh prunes are wheeled into the chamber, the fire is started and the temperature raised to 113° - 122° , or even 131° , if the prunes are dry. After half an hour the vents are opened slightly and heating proceeds for four or five hours with slightly increasing temperature. Towards the fourth hour the fruit is inspected and, if any dripping occurs, it is wheeled out. Towards the close of the wilting period the colour of the fruit should be a golden red. When this is attained the charge is wheeled out and cooled for at least an hour or, better still, for a day, as complete cooling is said to permit the retention of more weight in the fruit after drying.

For the second heating the temperature of the oven is brought to 130° F., and the truck wheeled in. The temperature falls to 104° F., and is raised to 158° or even to 167° F. The air vents are opened and the heating lasts for about four hours, after which the fruit is again thoroughly cooled.

The oven is then brought to 158° F., and the fruit again wheeled in. The cold-air inlet and the steam vents are partly opened, and, after three hours, when the prunes are seen to be well wrinkled, the heating is forced. The air inlets and vents are progressively closed, but permanent condensation on the glass is not permitted until towards the end of the process, when it is said to give an additional gloss to the fruit. It appears to be a general practice in most systems to force the heating somewhat towards the end of the process.

In concluding his account of the French methods of prune-drying, de Castella makes the important suggestion that it is possible that dehydrators might be so modified as to provide for that special cooking at the right stage of the process which is so marked a feature of the Agen method.

Grapes.

Grapes in California are usually dried in the sun in whole or divided bunches. The question of harvesting Muscat grapes has already been touched upon (p. 161). The rows of vines run from east to west, and the grapes on the drying trays are placed between the rows and tilted towards the south on a furrow of soil previously ploughed out. The bunches are cut with knives, and laid evenly on the trays on a single layer.

For dehydrating, and sometimes for sun-drying, the grapes are dipped in lye to remove the bloom and "check" the skins as for prunes. This hastens drying, and is especially useful when the crop is late. The dried product is also improved in appearance by dipping the fresh grapes in a cold solution of sodium carbonate, on the surface of which is a thin layer either of olive oil or, according to a recent American patent,¹³ a layer of oil expressed from the seeds of the grapes themselves.

In *sun-drying* the grapes are turned when about one-half to two-thirds dry, and stacked soon afterwards to finish at a slower rate.

In Australia a considerable amount of research has been carried out by Lyon ¹⁴ and others in order to standardise both the sun-drying of grapes and their treatment before drying, and the results have been embodied in a pamphlet issued by the Council for Scientific and Industrial Research for the Commonwealth of Australia. Here it is stated that the grapes

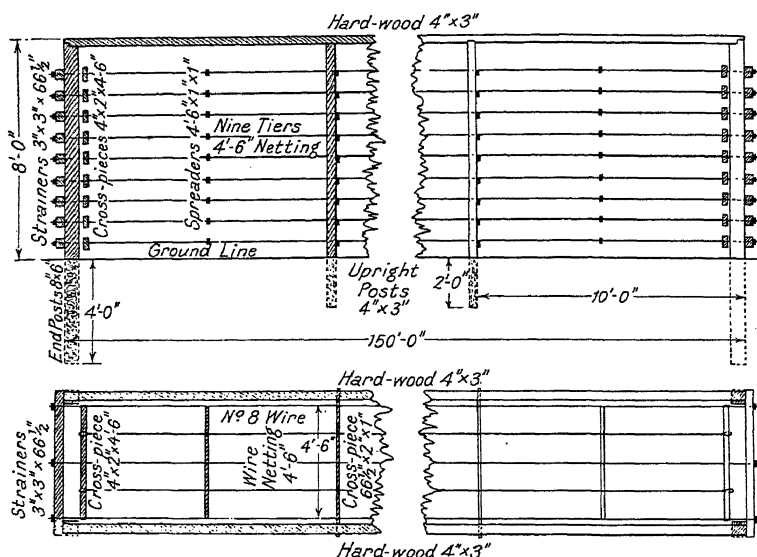


FIG. 32.—Rack-drying in Australia. Elevation (top) and plan (bottom) of rack (after Buerger),

are dried on permanent racks (Figs. 32 and 33) of wire-netting covered with zinc-roofing to prevent damage by summer rains. These racks are also usually provided with side-curtains of hessian to prevent rain from being driven on to the fruit by the wind.

Before being placed on the racks, the grapes are often dipped in lye or in a cold solution of potassium carbonate in which an emulsion of olive oil has been incorporated. The former has the effect of removing the bloom and cracking or

“checking” the skin slightly, thus hastening the drying process; the latter substitutes a thin oily coating for the bloom.

Lye may either be used boiling or at a lower temperature. If boiling, the strength is usually 3-4 lb. per 100 gallons, but it is advisable to start operations with a concentration of $2\frac{1}{2}$ lb. per 100 gallons and increase this by $\frac{1}{2}$ lb. at a time until results are satisfactory. The concentration of the dip is maintained by adding water until the original volume is restored, and 1 lb. of caustic soda for every 300 buckets of fruit dipped, but considerable caution should be exercised in adding the soda,

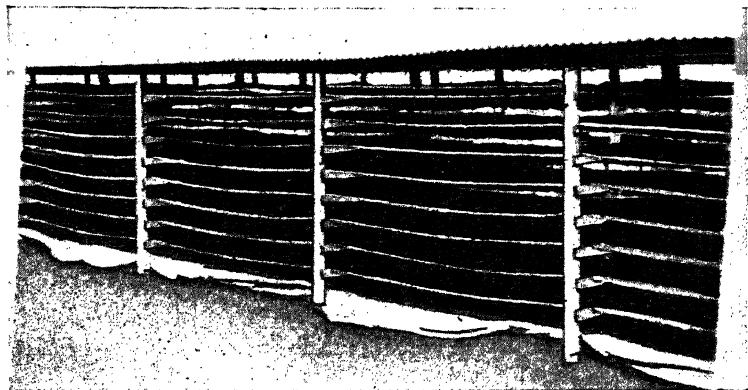


FIG. 33.—Rack-drying in Australia. Note hessian on bottom tier
(after Buerger).

otherwise the fruit may be damaged. “The ultimate guide for strength is the condition of the dipped fruit.”

The fruit is usually picked direct into perforated tins holding 14-16 lb. of fruit. A short immersion (one-and-a-half to two seconds) is sufficient, the tin of fruit being usually passed through the solution from right to left in a circular line. This ensures uniformity, that portion of the fruit which first enters the solution being the first to leave it. After dipping, the liquid is allowed to drain off quickly. Dipping at a lower temperature (190°-196° F.) is said to lessen the browning of the fruit caused by the boiling solution, but a slightly higher

concentration of soda ($3\frac{1}{2}$ - $4\frac{1}{2}$ lb. of caustic soda per 100 gallons of water) is required to remove the bloom satisfactorily. As in the case of the boiling lye, the correct strength of the solution must be maintained.

The cold dip of potassium carbonate and olive-oil emulsion does not appreciably affect the natural pigments of the grape; these are destroyed by exposure to the sun (bleaching) after dipping.

A solution containing approximately 5 per cent. of potassium carbonate (1 lb. to 2 gallons of water) gives the best results. For preparing the emulsion a solution containing 1 per cent. of potassium carbonate and a known amount of olive oil is stirred vigorously, the whole being made up to a definite volume. Of this emulsion an amount containing not less than $1\frac{1}{2}$ pints of olive oil is added to 50 gallons of the 5 per cent. solution of potassium carbonate.

According to the report, it is necessary to work with a strength of solution in excess of this minimum and to maintain it by adding, at frequent intervals, the equivalent of half a pint of oil per 50 gallons of dip if traces of bloom begins to appear on the dipped fruit after the correct period of immersion (about four minutes). The dip may be cleaned by filtering through coarse sand. In practice, a dipping solution, with two or three filterings and additions at full strength, may be used for 3000 or 4000 tins of fruit before it is necessary to discard it on account of stickiness.

Further essentials in connection with the drying of grapes, which apply after any one of these methods of dipping, are thorough draining and thin spreading on the racks. The best results are secured by building the racks on a north and south line and allowing the roof to overlap $1\frac{1}{2}$ -2 feet for shading. Spraying with a solution, similar to that used for the cold dip, is said to hasten the rate of drying and so preserve the quality; it is essential with cold-dipped fruit, except during very hot weather, when the rate of drying is satisfactory; it is advantageous after the "modified temperature" dip (190° - 196° F.)

in normal weather, and is essential on all fruit in showery or dull weather. The equivalent of $1\frac{1}{2}$ pints of olive oil per 50 gallons of spray is said to give the best results, but this may be increased or diminished by $\frac{1}{4}$ of a pint, according to the amount of oil showing on the fruits. In normal weather the first spray should be applied on the third day of the drying period, and thereafter at intervals of three days.

After the fruit is thoroughly dried it may be removed from the racks ¹⁵ by shaking, but this should only be done in settled weather. It is then spread thinly on hessian to attain uniformity of colour. Cold-dipped fruit requires two to four days to bleach, after which it should be washed, on a fine sunny day, by dipping, and again exposed on dry hessian until the desired degree of dryness is secured. The wash in general use consists of a solution of potassium carbonate ($2\frac{1}{2}$ lb. in 50 gallons of water), to which $1\frac{1}{2}$ pints of emulsified olive oil have been added.

With the boiling dip the drying period on a shaded rack in normal fine weather in Australia is nine to ten days. Cold-dipping lengthens the drying period by about 50 per cent., whilst the modified temperature dip gives an intermediate period. The first method is useful, therefore, if quick drying is required, as at the end of a season; the two latter may be used at the beginning or middle of a season.

Instruments necessary in carrying out this work are a Baumé hydrometer graduated from 0° - 15° , with a good open 5-inch scale and a suitable thermometer. The standard cold-dip solution gives a reading of approximately 5.7° Bé.

In *dehydrating*, Cruess states that grapes respond well to the parallel or concurrent system with an initial temperature of 200° F. and a finishing temperature of 160° - 165° F. Dipped grapes may also be dried in twenty or thirty hours by the counter-current system with a finishing temperature of 165° F. After drying they may, if necessary, be stemmed by machinery, and seeded.

Dates.

Dates are mostly grown in Northern Africa and Arabia, but there are now large plantations in California. In Egypt and Arabia a number of varieties are grown, and their preparation is a curing as well as a drying process.

The fruit is gathered when fully ripe, but before it has dried or mummified or begun to turn brown and soften. It is usually dried in the sun, either on rushes or rush mats, in layers about $2\frac{1}{2}$ inches deep, being turned once in three or four days. In some districts the writer has seen it stated that a hole is dug in the ground of a size to hold a date-leaf basket, with capacity for 300-400 lb. of dates. The basket is lowered into the hole, the dried dates are introduced a few at a time, and well-trodden down to a solid airtight mass by the bare feet of a workman until the basket is full. It is then drawn up and stored. After sixty to ninety days, during which time a slow curing or ripening goes on inside the mass, the flavour is said to be unsurpassed.

In other districts the dates are dried two to five days, and subsequently placed in heaps every night for eight to twelve days to heat and ripen. They are then packed in boxes containing 40 lb. each.

According to Cruess, in parts of California, where, owing to the climate, the dates mummify on the trees instead of ripening properly, they are picked before they show signs of hardening, and fumigated in a cabinet with carbon bisulphide ($\frac{1}{2}$ oz. to a cubic foot) for two hours, to sterilise the fruit and kill all insect life. The fruit is then placed in specially made, tight, wooden boxes which are kept three to five days in an ordinary poultry incubator to ripen at about 96° F. Cruess states that the dates go in dry and firm and come out soft, moist, and beautifully translucent, with a delightful odour, characteristic of the variety grown (Deglet Noor). The fruit is then graded and packed in fancy boxes. A temperature slightly below 100° F. for several days is said to give a better

result than a higher temperature for a shorter time. In other parts of the country the dates ripen sufficiently on the trees, and can be picked without the above treatment.

Figs.

The world-famous centre for the fig industry is Smyrna. The figs are allowed to ripen on the trees and fall to the ground, from which they are gathered and spread one layer deep on rushes. They are stirred daily, and removed as they dry (after two to four days). When dry they are stored in a heap in a store-room, and finally graded and sent to a packing establishment.

Figs are also grown extensively in California. In some districts "Calimyrna" figs (a variety of the Smyrna fig) are dipped in a solution containing 10 lb. of salt and 10 lb. of slaked lime per 100 gallons of water to remove some of the hairs from the surface, to improve the colour and soften the skins. Some Adriatic figs are similarly treated, and are also sulphured for three hours to bleach and sterilise them; the Calimyrna fig, however, is not sulphured.

Cruess states that in California the figs are often one-half to two-thirds dry on arriving at the drying yard, and can be stacked immediately after spreading on trays. This is important, as over-exposure to the sun toughens the skin and a product of better quality is obtained by drying the fruit entirely in the stack. The figs are dried until firm and until juice or syrup can no longer be expressed with the fingers.

Cherries.

Cherries are washed, the stones either removed by machinery or not as desired, trayed, steam-processed and dried, or they may be lye-dipped to crack the skins and, if of the white variety, sulphured for a short time. Black varieties need not be sulphured.

Berries.

Loganberries and raspberries require careful handling. If washed, this should only be done by means of a light spray of cold water. In California they are sometimes dried in the sun ; in other districts they are artificially dried.

Curing or "Sweating."

The process of curing dates has already been mentioned. With these it is accompanied by ripening changes and improvement in flavour. With many fruits it is merely a process for attaining an even distribution of moisture throughout the sample of fruit. This process may take several weeks, and is usually carried out in large closed bins, or the dried fruit is merely left in a large heap, turned occasionally, on the floor of a room from which insects and other pests are excluded.

CHAPTER X.

STORAGE OF DRIED FRUITS.^{16, 17, 18, 35.}

FRUITS properly dried and stored at the right degree of humidity keep well, but are subject to the attacks of insect pests. The most troublesome of these are the Indian Meal Moth (*Plodia interpunctella*), the Saw-toothed Grain Beetle (*Silvanus surinamensis*), and the Dried Fruit Beetle (*Carpophilus hemipteris*). The Fig Moth (*Ephestia cantella*) also causes damage similar to that of the Meal Moth. These insects all multiply rapidly, and not only penetrate and devour the fruit, but also render it unsightly through the débris to which they give rise. The moths are special offenders in this respect, since they spin copious webs.

In order to combat these pests, it is necessary to exercise scrupulous cleanliness and vigilance in all warehouses and packing sheds. It is highly probable that the processes of sulphuring, dipping and drying, in the case of artificially dehydrated fruit, kills all insects and their eggs, hence it follows that, if fresh insects can be prevented from gaining access to the fruit until it is packed in insect-proof packages, no trouble is likely to arise. The doors of store-houses, packing-houses, etc., should therefore be kept closed, gauze should be fastened over all windows and openings, and the rooms should be so constructed that they can be fumigated occasionally. If trouble is experienced several remedies may be adopted, viz. :—

- (1) Fumigation.
- (2) Heat treatment.

Fumigation.

The chief fumigants which have been tried are carbon bisulphide, carbon tetrachloride, hydrocyanic acid, and sulphur dioxide. Of these, carbon bisulphide is perhaps the most satisfactory, although it has the disadvantage of being very inflammable and rather poisonous. Carbon tetrachloride is neither inflammable nor very poisonous to human beings, but is less efficacious against insects than carbon bisulphide. Hydrocyanic acid is an exceedingly dangerous poison, and should only be used with the utmost care in special buildings by experienced persons. Sulphur fumes can only be used for fruits normally sold in the sulphured state.

In using carbon bisulphide the methods are similar to those adopted for fumigating grain. The carbon bisulphide (4-8 lb. per 1000 cubic feet)²⁸ is placed in shallow containers at the top of the bin or storehouse in which the fruit is kept, such storehouses being, of course, made as airtight as possible. The vapour of the volatile liquid, being heavier than air, in sinking downwards penetrates thoroughly into all the crevices in the material to be fumigated. When correctly carried out, the method is effective, but it must be remembered that carbon bisulphide is very inflammable and explodes when mixed with air and ignited. Fumigation with carbon tetrachloride is carried out in a similar manner.

Hydrocyanic acid gas is a very powerful insecticide, but has not the penetrating power of the previously mentioned materials. Fumigation with it can be carried out by methods similar to those used for fumigating greenhouses and nursery stock. The material to be fumigated is brought into a room which can be tightly sealed and the gas is generated by bringing sulphuric acid into contact either with sodium or potassium cyanide * by means of a device operated from outside (about

* Certain firms now undertake fumigation with prussic acid in specially erected buildings. The method consists in spraying the pure acid into the building from cylinders, the work being carried out by experienced persons provided with gas masks. This method would have many advantages over that described in the text.

1 oz. of sodium cyanide or $1\frac{1}{2}$ oz. of potassium cyanide, $1\frac{1}{2}$ fluid oz. of sulphuric acid, and 5 fluid oz. of water is used for every 100 cubic feet of space). After an hour the doors and ventilators of the room can be opened, but it must not be entered for several hours. The operation involves risk and, as already stated, should only be carried out by experienced persons.

Sulphur dioxide may be used for fruits like apricots, pears or peaches which have already been sulphured. These are treated for four to twelve hours in the fumes of burning sulphur. According to Cruess, a method known as vacuum fumigation has been used in recent years by the Federal and State authorities in the United States of America. The fumigating chamber is made of steel plates, and, after being charged with fruit, can be sealed and evacuated. The fumigant (usually carbon bisulphide, mixed with carbon dioxide) is then drawn in and remains in contact with the fruit for a stated period (usually one hour). Such a method is rapid and safe, and intimate contact between dense material and fumigant is ensured; the fumigant can also be rapidly and thoroughly withdrawn by suction after the treatment.

Roark and Cotton, of the U.S.A. Department of Agriculture and, later, Thomas²⁰ have experimented with a mixture of ethylene dichloride (3 parts), and carbon tetrachloride (1 part by volume), using 14 lb. (5 quarts of the mixture) per 1000 cubic feet of space. Thomas worked at air temperatures above 70° F., and found that treatment with this mixture for twenty-two hours, in perfectly air-tight compartments, sterilised dried fruit so far as *Plodia interpunctella* was concerned. He considers that the same result might reasonably be expected with other insects, although his results were not quite satisfactory for the eggs of the less serious pest *Silvanus surinamensis*. The mixture is more potent than carbon tetrachloride, and is neither dangerous to workmen nor inflammable, but its odour is liable to persist after treatment, and it vaporises slowly. More recently, Roark and Cotton,¹⁹ Back, Cotton and Young³⁴ and

Thomas have reported that still better results are obtained by fumigation for twenty hours with *ethylene oxide*, using 2 lb. per 1000 cubic feet of space. This fumigant is not dangerously explosive or inflammable at this concentration, is non-poisonous to human beings, harmless to the food, and very volatile (B.P., 51° F.). Its potency is increased for certain products (nuts) by the addition of seven to nine times its weight of carbon dioxide, such a mixture being used at the rate of 10 lb. per 1000 cubic feet for twelve hours or 10 lb. per cubic foot for 1½ hours under vacuum. Roark now regards ethylene oxide as the ideal fumigant for foodstuffs. It is more toxic than hydrocyanic acid to some insects and much less toxic to man and the slight residue left behind is believed to be harmless, odourless and does not injure the food.

Heat Treatment.

Some dried fruits, like prunes, peaches, raisins or figs, are dipped on a conveyor in boiling water or in a boiling solution consisting of salt 50 lb., sodium bicarbonate 3-4 lb., and water 150 gallons. A dry heat of 125°-150° F. for several hours is also said to kill all insects likely to attack dried fruits. This means that the goods can be passed again through a dehydrator or heated in a chamber fitted with steam coils. Sterilised products must be allowed to dry and then be packed immediately, preferably in containers which have also been sterilised to free them from the eggs of insects.

Insect-proof Packages.

It has already been pointed out that packing-rooms should be guarded as far as possible with gauze, etc., to exclude insects. Care should also be exercised in the choice of packages. Sealed tins exclude insects perfectly and are moisture-proof, but material must either be dry before being packed in them or the package must be sterilised, otherwise it will form an admirable chamber in which moulds can develop. The

ordinary wooden or cardboard boxes are not insect-proof, but can be made so, to a large extent, by using a lining of waxed paper which is sealed after filling. Such packages, however, are not quite moisture-proof, and there is danger of moulds developing in them in damp store-houses.

Cold Storage.

A means of arresting the growth of insects, although it does not destroy them, is cold storage. This is, however, attended with difficulties, when the material is removed from the store, owing to the inevitable condensation of moisture upon it.

CHAPTER XI.

PRINCIPLES OF DEHYDRATION.^{1, 24, 26, 28, 29, 30, 31.}

It is well to commence this chapter by quoting the following statement by Caldwell²¹: "Success in drying . . . depends upon the employment of sound, ripe fruit of unimpaired table quality, the use of suitable means for preventing oxidation and other chemical changes during the drying process, the employment of a temperature so regulated that the material may not be injured by excessive heating and so maintained that the opportunity for fermentation and spoilage is avoided, and the provision of an adequate circulation of air to carry away the escaping moisture. Failure to give proper attention to any one of these factors will result in the production of an inferior grade of product or in the total loss of the material used."

Although it is not proposed to go into details concerning the different types of dryers and their construction, it is necessary to devote some space to the main principles involved in dehydration.

The type of dryer, which has largely superseded all other forms for large-scale commercial drying of fruit, is the forced-draught tunnel dryer or air-blast dehydrator. Earlier forms are kiln driers (still extensively used for apples), stack dryers, in which the material enters the dryer on trays at the top of a vertical shaft and is removed at the bottom, and tunnel dryers, such as the Oregon tunnel. Both of the latter types make use of the natural draught caused by the tendency of heated air to rise, the source of heat being at the lowest part of the system.

For products, which should be dried at low temperatures, vacuum dryers, in which the drying is carried out under reduced pressure, have been constructed, but these are expensive, and not in general use for fruit.

In 1923 Caldwell emphasised the importance of rapidity in drying, since this minimises damage by fermentation and autolytic changes, and increases the capacity of the dryer. At the same time, however, he was inclined to favour the natural-draught types, because the defects in forced-draught driers, viz. the tendency towards case-hardening due to too rapid drying, wastage of fuel due to too rapid movement of air, coupled with the greater initial outlay and skill required, seemed to outweigh the advantages likely to arise from their use.

These obstacles have now been largely overcome through the practice of re-circulating a proportion of the air, and the forced-draught dryers are now recognised as the most efficient of all. They are rapid in their action, capable of a high degree of temperature and humidity control, and produce a product of high quality.

The essential features of this type are as follows :—

- (1) A single or multiple chamber ²⁵ which often takes the form of a tunnel in which the fruit is placed.
- (2) A source of heat.
- (3) A fan for drawing heated air through an air duct and driving it over the material to be dried.
- (4) An arrangement of dampers for returning a proportion of the heated air from the drying chambers to the heater.

The fruit to be dried is usually spread on trays (some dryers work on a conveyor system), with slatted bottoms, which are stacked on trolleys so that air can pass freely between them, as already indicated (p. 162). The arrangement is such that when a trolley-load of fresh fruit is pushed into the dryer at one end, another carrying the finished product is withdrawn at the other.

The trolleys, with their loads of trays, are of such a size that they fill the cross-section of the tunnel almost completely, so that the opportunity for air to pass through without coming into intimate contact with the fruit is reduced to a minimum.

The following detailed description of two types of dehydrating plants is given in a Report on the Apple Industry in Tasmania.²² In Tasmania the kiln type of dryer has been in use, but the report suggests two other types as being much more suitable, viz. :—

- (1) The batch type of dehydrator.
- (2) The tunnel type.

(1) The Batch Type.

This has a floor space of 12 feet \times 12 feet, and is 6 feet high. It has an output of 175,000 lb. of dried apples in a season when operated six days a week in two shifts per day. It is constructed of brick, concrete or steel, suitably insulated to minimise heat losses. The dehydrating chamber is 10 feet \times 10 feet, surrounded on two sides by a passage 2 feet wide. Circular flues carrying the furnace gases pass through this passage and the dehydrator can be adapted for any type of fuel, but oil is considered most suitable.

A fan draws the drying air at the rate of 2500 feet per minute over the heated pipes in the passage, and then over the trays, which can be made of wood, lacquered wire-netting or screen, each measuring 4 feet \times 2 feet 6 inches, and placed on horizontal arms carried by a vertical, slowly rotating spindle, driven by gearing from above. The rotation of the trays gives decreased drying time and uniform drying conditions. The air, after passing over the trays, contains a high percentage of moisture and impinges on the two front doors of the dehydrator, which are suitably cooled. On the inside of these doors the moisture of the air is condensed and drains away at the front bottom corner. The air then passes to the right-angled partition, and is drawn by the fan along the side and

back of the dehydrator, being again heated. Necessary port-holes for the admission of fresh air are provided, and a hair-hygrometer is used as a control for humidity.

(2) The Tunnel Type of Dehydrator.

In the tunnel type of dehydrator, drying is carried out in a long, rigidly constructed chamber or tunnel, fitted with airlock doors at each end and heated below the floor and, possibly, at the sides by the products of combustion of wood, oil, coal or gas. The fruit to be dried is placed on trays, usually made of wood, since other material is affected by fruit acids. The trays are then built up one upon another on a truck. They are usually placed in two piles with spaces in between each tray for the passage of heated air. The trucks are pushed through the airlock doors into the drying tunnel. A number of precisely similar trucks in the tunnel complete its charge, so that when one truck is pushed in, a similar truck carrying dried fruit is pushed out through the airlock at the other end. The tunnel should be worked continuously to obtain the most economical results.

The air for drying is re-circulated continuously by a fan, and additional outside air is admitted to keep the humidity (of the out-going air) approximately constant at 65 per cent.* The smallest type of tunnel dryer recommended in this report is 62 feet long,† 10 feet wide, and 8 feet high (overall dimensions). The tray area of such a dryer is 3000 square feet, and with a spread of apple rings of 2 lb. per foot the tunnel would have an output of 10 cwt. of dried apples in six hours, or 40 cwt. per day.

It is stated that the tunnel type of dehydrator is economically

* This figure is given as the percentage of humidity in the air *leaving* the dryer by Cruess and Nichols, Powers, Gross and Noel.

† It must be noted here that Nichols and Christie do not consider that more than 30 feet of the length of a tunnel should actually be used for drying apples. This would make the length (62 feet) recommended in the report excessive. The air velocity should be 700-800 feet per minute.

possible only with large outputs and continuous operation. The batch dehydrator, on the other hand, can be constructed in much smaller units, and is generally more flexible. It is considered that both types are cheaper to run than the kilns, but precise figures of costs were not available at the time of publication of the report.

Heating Systems.

It is economical to have more than one tunnel per heating unit, of which several types are used, viz. :—

- (1) Direct heat.
- (2) Direct radiation.
- (3) Indirect radiation.

In the first system the gaseous products of combustion, mixed with hot air, pass over the material to be dried. With this system combustion must be complete, and the fuel carefully chosen so that no soot, dust or noxious substances such as arsenic, are deposited on the food. This system gives the highest thermal efficiency, but requires careful control so that over-heating, case-hardening and caramelisation do not occur.

In the second method the air is either heated by passing over pipes carrying the hot furnace gases or, alternatively, the air may be drawn through pipes heated from the outside. This system gives a thermal efficiency nearly as high as the first, and there is no danger of deposition on the fruit, but again care is needed to guard against over-heating.

The third system consists in heating the air by means of batteries of steam pipes or radiators. This is the most expensive system to instal, and has the lowest thermal efficiency, but permits of the most accurate control over temperature. There is also less risk of fire with this type.

The Fan.

The fan used for circulating the air through the dryer must be capable of imparting to it a considerable velocity against a

high frictional resistance. Nichols and co-workers recommend a turbine fan with forty-eight to sixty-four or more blades of short radial length. It may either be installed so as to draw air over the heaters and impel it into the tunnel, or it may exhaust air from the tunnel and impel it over the heaters. Either position is considered satisfactory. Intimate contact of the air with the fruit is essential, and involves frictional resistance. Such resistance is kept as low as possible by having large air-ducts and shaping them correctly so as to avoid sharp elbows.

Re-circulation and Case-hardening.

It is obvious that sufficient air must leave the dryer to carry away the moisture, but re-circulation of a proportion of the air which is re-heated along with air drawn from outside has been found to be an important factor in raising the thermal efficiency of the dryer and in preventing case-hardening. It has already been pointed out that, as a general rule, the more rapidly products are dried the better their quality, provided that they have not been injured by high temperature. The rate at which fruits can be dried is, however, limited by the rate at which water can diffuse to their surface. If conditions are such that the surface layers lose water more quickly than it reaches them from inside, these layers become hard, leathery and relatively impervious, so that evaporation is permanently impeded. This is overcome by not having the initial temperature of the air too high and by increasing its humidity, the latter condition being largely controlled by varying the amount of air re-circulated by means of dampers. In general, the temperature of the air entering the drying tunnel should not exceed 160°-170° F., and the humidity at the exhaust end should be about 65 per cent. Cruess regards a re-circulation of 75 per cent. of the air as desirable for many fruits and vegetables which dry rapidly. As a general principle, however, Carrier²⁴ has shown that the higher the temperature and the greater the

percentage of air re-circulated the greater the efficiency of the dryer.

Velocity of the Air.

The rate of drying increases with the velocity of the air passing through the tunnel. Too high velocities, however, decrease the thermal efficiency of the dryer owing to the greater air-losses entailed, and unduly increase the work of the fan so that expenditure of power becomes a consideration of importance. Moreover, with light materials high velocities are obviously impracticable. According to Nichols and co-workers, air-velocities of 600-800 linear feet per minute are satisfactory in tunnel dryers, and lower velocities in compartment dryers. Cruess states that the velocity should not exceed 1000 feet per minute, nor fall below 300 feet. He points out that the Carrier ²⁴ equation for the relation of velocity to the rate of drying, viz. :—

$$W = 0.093 \left(1 + \frac{v}{230} \right) (e' - e),$$

where W = pounds of water evaporated per square foot of drying surface per hour,

V = velocity of air over drying surface in feet per minute,

e' = vapour pressure of water corresponding to its temperature,

e = vapour pressure of the surrounding atmosphere,

does not apply to materials like fruits for high velocities, although it applies fairly well with moderate velocities and in the earlier stages of drying, when the proportion of free water is high.

The velocity of the incoming air may be measured by means of an anemometer, and both static or frictional pressure and the total pressure can be measured inside the tunnel by means of a combined Pitot and static tube placed in the path of the

air.* The difference between total and static pressures gives the velocity pressure, and from this the linear velocity of the air can be calculated by using the formula

$$V = 4101 \sqrt{p},$$

where p = the velocity pressure in inches of water (found by measurement),

and V = velocity in feet per minute.

Also $V \times$ the free cross-sectional area of the tunnel in square feet = No. of cubic feet of air measured at 60° F. passing through the tunnel per minute.

Counter-current and Con-current or Parallel Systems of Drying.

When the direction of the air current is opposite to the flow of the material to be dried, the system is said to be counter-current; when the flow of air and material is in the same direction, the system is known as con-current or parallel.

In the first system, which is the one in most general use, the discharge end (for fruit) of the dryer is the hottest. It is necessary to use this system with fruits like prunes which drip badly if the initial temperature is too high, but there are certain drawbacks attached to it because a high temperature and low humidity at the end of the process favour case-hardening and scorching.

In the second system the process is started in hot dry air and completed at a moderate temperature in moister air. Cruess favours this system for small fruit, grapes, and sliced fruit like apples, because (a) evaporation is most rapid just when the fruit is in a condition to give up its water most rapidly, (b) the fruit is more nearly at the temperature of the wet bulb of the thermometer throughout the process, and therefore stands less chance of scorching, case-hardening or

* See E. Ower, "Measurement of Air Flow," Chapman & Hall, London, 1927.

over-drying, and (c) less heat is carried out with the fruit and trolleys, since they are withdrawn at a lower temperature.

Some Guiding Principles in Working and Constructing a Typical Air-blast Dryer.

Apart from considerations of case-hardening and scorching, the rate of drying is governed by the temperature to which the fruit is raised by the passage of the hot air over it and by the velocity and humidity of the air.

According to Nichols and co-workers, general experience in drying prunes has shown that the temperature of the incoming air should be about 160° F., which agrees with the figure given by Cruess. Its humidity should be about 20 per cent., the fall in temperature in passing through the tunnel about 35° F. (Cruess says 40° F.), and the humidity of the air as discharged 60-65 per cent. Under these conditions the period of drying will not exceed twenty-five hours, and about 35 lb. (drying ratio 2.8 : 1) of dried prunes will be obtained from 100 lb. of fresh prunes. Departures from these figures will be necessary for other fruits, but since such departures should be within the range of flexibility of the dryer, the figures for prunes may be taken as a working basis for construction.

Other essential figures are as follows, viz. :—

(1) The Quantity of Fresh Material required to be Handled in a Given Time.

This figure is necessary in order to calculate the number of trays and trucks required, assuming an average load of 3 lb. of fresh fruit per square foot of tray surface. Nichols and co-workers assume that the trays will be 3 feet square, that each truck should hold two stacks of trays 25 high, and thus offer 450 square feet of spreading surface. For a daily intake of 7 tons of prunes the dryer should hold eleven of these trucks at a time, giving a total spreading surface of 4950 square feet.

(2) The Free Cross-sectional Area of the Tunnel.

The trays are reckoned to be 1 inch in thickness and 2 inches are allowed between each tier. From this it is calculated that there are 25 square feet of cross-sectional area through which air can pass, provided that the spaces on all sides of the trucks are baffled. This figure can be used in calculating air velocities when the volume of air passing through the dryer in a given time is known.

(3) The Quantity of Water to be Evaporated in Pounds per Unit of Time.

This is found by subtracting the weight of finished from the weight of fresh fruit over a given period, and calculating the loss of water in pounds per minute. Thus, if 7 tons are to be dried in twenty-four hours, the rate of evaporation on the basis of the drying ratio already given must average 6.32 lb. per minute.

(4) The Heat Required for Raising the Temperature of the Fruit and for Evaporating the Water at the Necessary Rate.

Since the fruit is raised through approximately 100° F., it is sufficiently accurate for this purpose to say that 100 B.T.U. are required for the first step per pound of water evaporated. It is known that approximately 1000 B.T.U. are required to evaporate 1 lb. of water. Hence the heat required per minute in evaporating 6.32 lb. of water will be

$$(1000 + 100) \times 6.32 = 6952 \text{ B.T.U.}$$

A closer approximation, according to Butcher,²⁶ would be

$$1080 \times 6.32 = 6825 \text{ B.T.U.}$$

(5) Heat Losses.

Heat losses are caused by incomplete combustion of the fuel, the escape of hot flue gases, radiation from the dryer,

leakage of air from the dryer through cracks, opening doors, etc., removal of heated material, trucks, etc., the initial heating of trucks and dryer and the necessary discharge of a proportion of the air. These quantities are exceedingly difficult to compute, but some of them may be arrived at roughly by considering the specific heats and coefficients of heat-transmission of the various materials. Butcher has given the coefficient of heat-transmission of the constructional materials used in dryers (see Table XXII.). The heat radiated from the dryer will depend largely upon its construction, insulation, etc.

If the dimensions of a given dryer are

Length	45 feet
Width	4 "
Height	5 "

the internal surface, including doors 40 square feet, will be approximately 670 square feet. To calculate the losses through radiation, let us assume for the sake of example that the mean temperature difference between the inside and outside air is 80° and that the tunnel is built of 14-in. brickwork, we have

$$670 \times 80^{\circ} \times 0.28 = 15,000 \text{ B.Th.U. per hr.,}$$

which is equivalent to 348 cub. ft. of drying air per minute, when dropping 40° F., or 394 cub. ft. for 35° F.

The loss due to air, leaving the dryer, can be estimated if the quantity and temperature of this air are known (specific heat of air at constant pressure = 0.238).

TABLE XXII.

COEFFICIENTS OF TRANSMISSION OF HEAT IN B.T.U. PER SQUARE FOOT PER $^{\circ}$ F. PER HOUR FOR VARIOUS CONSTRUCTIONAL MATERIALS (*after Butcher*).

Brick walls, $4\frac{1}{2}$ inches thick	0.50
" " 9 " "	0.36
" " 14 " "	0.28
Concrete roofs, $4\frac{1}{2}$ inches thick	0.65
" " 9 " "	0.47
" " 14 " "	0.36
1-inch board with 2 inches sawdust filling	0.13
Sheet iron with 1-inch cork board in solution	0.30

From the total heat requirements and the initial data (pp. 198, 199), it is possible to calculate the quantity of air necessary to carry that heat; the quantity of fuel necessary to generate it can be calculated from calorimetric tests.

In calculating the quantity of air required, it is usual to consider either the weight or the volume of air, measured at 60° F., which enters the dryer in a given time. According to Butcher the weight of 1 cubic foot of dry air at 60° F. is 0.0761 lb., and its specific heat at constant pressure is 0.238. From this, the amount of heat required to raise 1 cubic foot of air through 1° F. is $0.0761 \times 0.238 = 0.01811$ B.T.U. Conversely, 1 cubic foot of air dropping 1° F. will give out 0.01811 B.T.U.

Taking the figure 1080 B.T.U. as the amount of heat necessary to raise 1 lb. of water from 60° to 160° F., and converting it to vapour, we have

$$\frac{1080}{0.01811} = 59,635, \text{ or, approximately, } 60,000 \text{ cubic feet of air dropping } 1^{\circ} \text{ F.,}$$

$$\text{or } \frac{60,000}{35} = 1714 \text{ cubic feet dropping } 35^{\circ} \text{ F.}$$

For 6.32 lb. per minute this will be 10,832 cubic feet of air per minute measured at 60° F. If we allow from 3000 to 5000 cubic feet per minute for heat losses, we have a total air requirement of approximately 14,000 to 16,000 cubic feet per minute for a dryer of this type or 2.8 to 3.2 cubic feet per minute per square foot of drying surface.

It will be noticed that the humidity of the entering air has not been considered from the point of view of these calculations. It is true that this will have some effect on the rate of drying, and that it influences case-hardening, but since the amount of air required to carry the heat is much greater than the amount of air required to carry the evaporated water, and since the air in the dryer is at no time near the saturation point, the effect of the initial humidity is relatively negligible.

The overall efficiency of the dryer can be calculated from

TABLE XXIII.
DETAILS OF DEHYDRATION OF FRUITS AND VEGETABLES (after Nichols, Powers, Gross and Noel).

Product.	Trimming, etc.	Yield after Trimming, etc., Per Cent.	Form for Drying.	Approximate Load on Trays, Pounds per Square Foot.	Pre-treatment.	Time of Sulphuring, Dipping, etc. Minutes.	Drying Temperatures, Degrees F.	Average Drying Time, Hours.	Preferred Moisture Content, Per Cent.	Characteristics of Dried Product.	Keeping Qualities.	Yield From Fresh-prepared Fruit, Per Cent.	Yield from Fresh Fruit, Per Cent.
Apples	Peeled, cored, trim	65-75	Cube or slice	1.5	Sulphur	15-30	140-160	6-10	10-15	Dry, stringy	Good to fair	16-19	10-15
Apricots	Washed, halved, stone	90-94	Dried in halves	2.0	"	15-25	135-155	10-20	15-20	Slightly moist to leathery	"	17-20	15-19
Bananas	Stem, peeled	52-57	Whole or sliced	1.0	"	15-30	140-160	10-20	15-20	Sticky, limber	"	28-31	13-18
Cherries (unpitted)	Washed, stem	97-99	Whole	1.0	None or steam	0-2	135-160	8-12	15-20	Slightly moist to sticky, limber	Excellent	25-30	24-30
Cherries (sweet, pitted)	"	77-83	"	1.0	"	0-2	135-160	8-12	15-20	Slightly moist to sticky, limber	"	24-28	18-24
Cranberries	"	100	Chopped	0.8	"	0-2	135-150	4-8	5-10	Dry, tough to brittle	Excellent to good	10-14	10-14
Plums	Washed (optional)	100	Whole	3.0	Boiling lye dip (1-3 % lye), rinse after dipping	1-3	135-160	10-20	15-20	Skin dry, glossy; flesh slightly moist	Good	24-27	24-27
Grapes	Stem and seed after drying	80-90	Subdivide clusters	3.5	Boiling lye dip (1-3 % lye), rinse after dipping	1-3	150-180	20-30	15-20	Skin dry, glossy; flesh slightly moist	Excellent to good	26-30	21-27
Loganberries	Washed (optional)	100	Whole	1.2	None	140-150	10-15	10-15	10-15	Dry, but should not crumble	Excellent to good	15-18	15-18
Peaches	Halved, peeled, pit	85-95	Halved	2.5	Sulphur	15-30	145-155	15-24	15-20	Dry, leathery	Good to fair	17-21	14-19
Pears	Peel, halved, core	75-80	"	3.0	Boiling lye dip	1-3	140-150	15-24	10-15	Skin dry, flesh slightly moist	"	17-20	12-17
Prunes	Graded for size	100	Whole	3.0	"	145-160	20-30	15-20	15-20	Dry, but should not crumble	Excellent to good	33-38	33-38
Raspberries	Washed (optional)	100	"	1.0	None	140-150	10-15	10-15	10-15	Dry, but should not crumble	Good	16-20	16-20
Rhubarb	Trim stalks, wash	55-60	Slice	1.0	Steam	2-4	140-150	10-15	5-10	Dry, tough	"	6-9	2-7

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TABLE XXIV.
RECOMMENDED METHODS FOR DEHYDRATION OF VARIOUS FRUITS (COUNTER-CURRENT METHOD).

Variety of Fruit.	Pounds per Square Ft.	Hours Sulphured.	Maxm. Temp. at end of Drying Period.	Desirable Humidity in Dehydrator at end of Drying Period.	Drying Time by Counter-current Method.	Remarks.
			°F.	Per Cent.	Hours.	
Apples . . .	2	$\frac{1}{2}$	165	5-10	8	Peeled and sliced or cubed.
Apricots . . .	2	1	160	10	12	Halves ; unpeeled.
Bananas . . .	1-2	$\frac{1}{2}$	165	5-10	12-18	Peeled, cut in half lengthwise.
Cherries :—						
Black tartarian	2-3	0	170	10-25	8-12	Lye dipped.
Royal Anne . .	2-3	$\frac{1}{4}$	170	10-25	8-12	"
Figs . . .	2-3	1	160	5	10	One side cut and figs spread open.
Grapes :—						
Muscat . . .	3 $\frac{1}{2}$ -4	0	160	5	24	Lye dipped.
Seedless . . .	3 $\frac{1}{2}$ -4	1	160	5	16	"
Wine . . .	3 $\frac{1}{2}$ -4	1	160	5	20	"
Loganberries . .	1 $\frac{1}{2}$ -2	0	160	10-25	10-15	Untreated.
Peaches . . .	3	1	150	20-30	24	Not peeled.
" . . .	3	1	150	20-30	16	Lye "
Pears . . .	3	24	145	30-40	48	Halves unpeeled.
" . . .	2	$\frac{1}{2}$	150	10-20	6	Peeled and sliced.
" . . .	2	1	150	10	16	" , cored.
Prunes :—						
Italian . . .	2 $\frac{1}{2}$ -4	0	170	20-30	24	Lye dipped.
French . . .	2 $\frac{1}{2}$ -4	0	165	20-30	24	"
Imperial . . .	3-4	0	165	20-30	30-36	Lightly dipped.
Raspberries . .	1 $\frac{1}{2}$ -2	0	170	10-25	8-12	Untreated.
Strawberries . .	1 $\frac{1}{2}$ -2	$\frac{1}{2}$	160	10-25	24	Stemmed.

Reproduced by courtesy of the McGraw-Hill Book Co., Inc., from "A Laboratory Manual of Fruit and Vegetable Products," by W. V. Cruess and A. W. Christie.

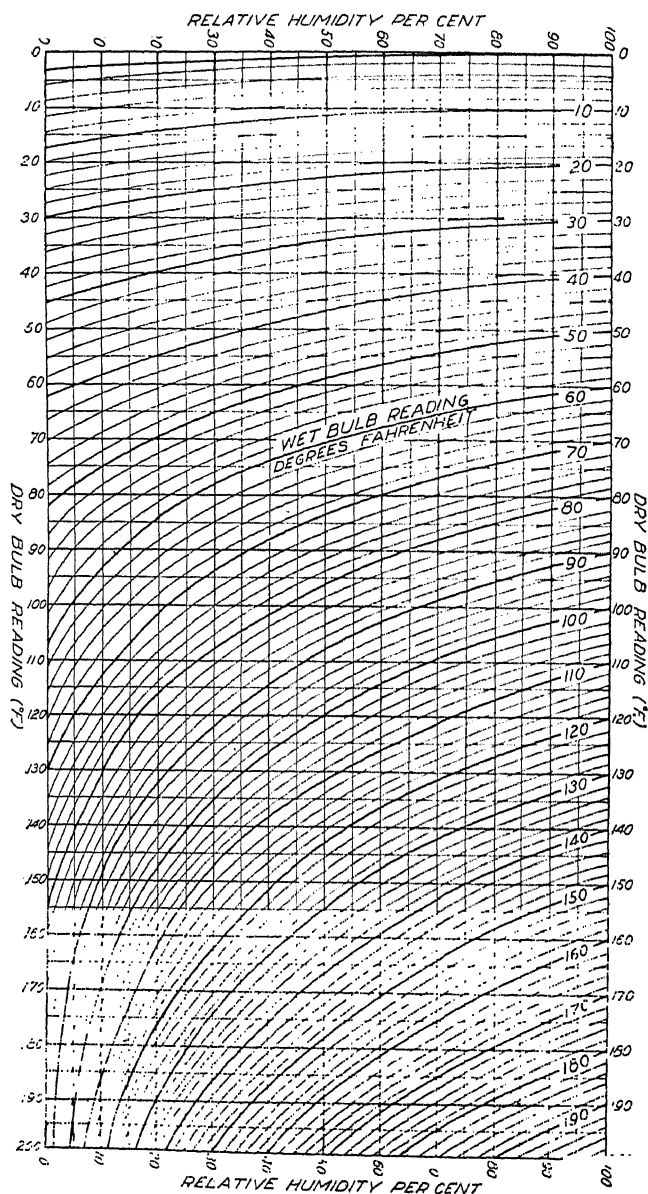


FIG. 34.—Relative humidity from dry and wet-bulb readings. [By permission of the United States Department of Agriculture.]

the relation between the number of B.T.U. generated by the

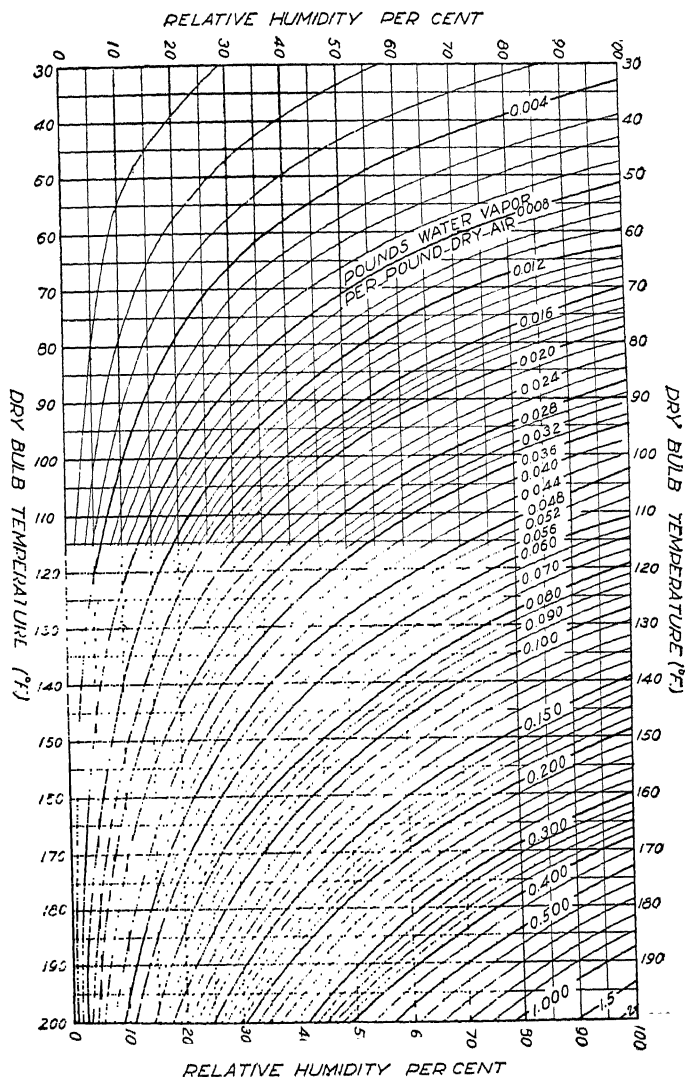


FIG. 35.—Pounds of water vapour per pound of dry air. [By permission of the United States Department of Agriculture.]

fuel and the number of B.T.U. represented by the weight of water evaporated in a given period. The efficiency of the

heating arrangements may be found by comparing the heat derived from the fuel with the heat used in raising the incoming

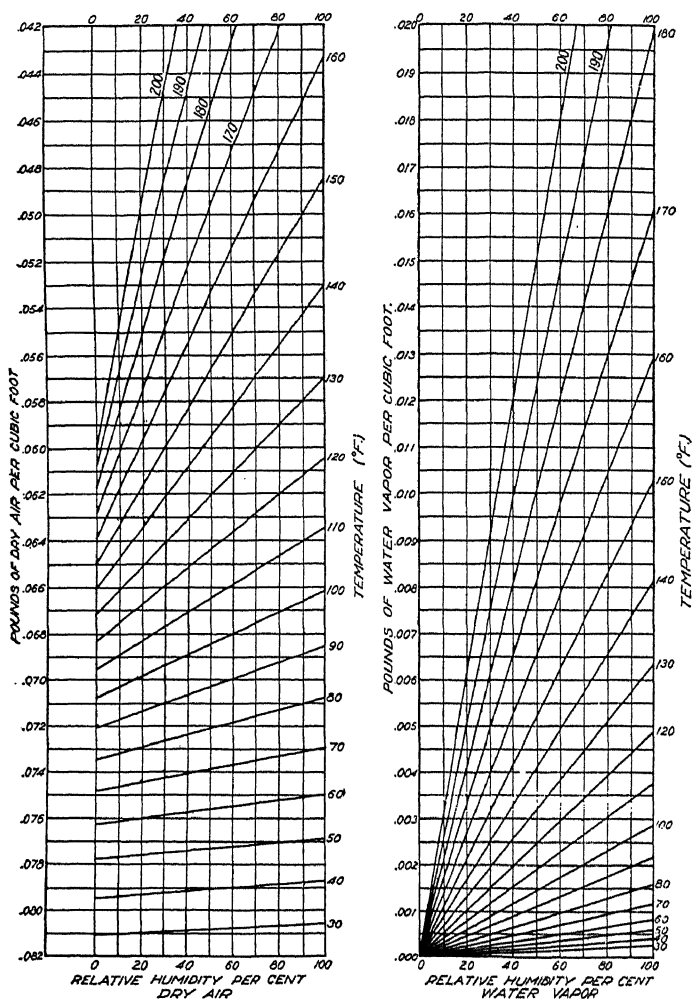


FIG. 36.—Pounds of dry air and of water vapour per cubic foot, at a barometer reading of 29.921 inches. [By permission of the United States Department of Agriculture.]

air from atmospheric temperature to the temperature at which it enters the dryer.

Tables for Drying.

Tables XXIII. and XXIV. give the methods for drying recommended by Cruess and Christie ²⁷ (Table XXIII.) and Nichols, Powers, Gross and Noel (Table XXIV.). It will be noted that these authorities differ considerably in certain of their recommendations, partly, no doubt, because of differences in starting and finishing temperatures, and partly because dryers are by no means standardised, and each has its individual peculiarities. The sulphuring periods given, particularly by Nichols, Powers, Gross and Noel, also are admittedly too short in many cases [cf. Nichols and Christie, ref. No. 10], and should be compared with those recommended in the text under the various fruits. Comparison of the two tables, and the various figures in the text, however, gives some idea of the need for standardisation, and would form a starting-point for practical working to be modified subsequently according to experience and individual judgement.

Humidity Charts.

Figs. 34, 35 and 36 are charts showing the Relative Humidities corresponding to wet and dry bulb temperatures, pounds of water vapour per pound of dry air, and pounds of dry air and water vapour per cubic foot at a pressure of 29.921 inches. Such charts are essential in any calculations connected with the working of a dehydrator.

REFERENCES.

DRYING, ETC.

- 1 CRUESS, W. V., "Commercial Fruit and Vegetable Products," McGraw-Hill Book Co. Inc., 1924.
- 2 NICHOLS, P. F., POWERS, R., GROSS, C. R., and NOEL, U.S.A. Dept. Agric. Bull. 1335, 1925.
- 3 CULPEPPER, C. W., and CALDWELL, J. S., "The Relation of Atmospheric Humidity to the Deterioration of Evaporated Apples in Storage," *J. Agric. Res.*, 1927, 35, 889.

208 PRINCIPLES OF FRUIT PRESERVATION

- 4 ANDERSSSEN, F. G., "Sulphur Dioxide in Dried Fruits," *Sci. Bull.* 84, Union of S. Africa Dept. of Agric.
- 5 ARCHBOLD, H. K., "Chemical Studies in the Physiology of Apples. II. The Estimation of Dry Weight and the Amount of Cell Wall Material in Apples," *Ann. Bot.*, 1925, 89, 109.
"Chemical Studies in the Physiology of Apples. VIII. Further Investigations of the Methods of Determining the Dry Weight of Apple Pulp," *Ann. Bot.*, 1928, 42, 29-38.
- 6 WIEGAND, E. H., and BULLIS, D. E., "A Method for Testing Moisture in Dried Prunes," *Oregon Agric. Coll. Expt. Sta. Circ.* 82, June, 1927.
- 7 MONIER-WILLIAMS, G. W., "The Determination of Sulphur Dioxide in Foods," Rep. No. 43 on Public Health and Medical Subjects, British Ministry of Health, 1927.
- 8 WARTHA, A., "Silver Nitrate Test for Sulphur Dioxide : Determination by Distillation into Iodine, and Titration," *Ber.*, 1880, 13, 657.
- 9 BIOLETTI, F. T., "Relation of Maturity of Grapes to the Quantity and Quality of the Raisins," *Proc. Intern. Congress Viticulture*, 1915.
- 10 NICHOLS, P. F., and CHRISTIE, A. W., "Drying Cut Fruits," *Univ. Cal. Agric. Exp. Sta. Bull.* 485, 1930.
- 11 "The Sulphuring of Apricots" (Committee), *J. Dept. Agric. S. Australia*, 1929, 33, 240.
- 12 DE CASTELLA, F., "Prune Drying," *J. Agric. Victoria*, 1930, 28, 497, 615, 734.
- 13 FORREST, T. W. W., "Raisins Sprayed with Oil while Hot," United States Patent 1,726,816 (1929).
- 14 LYON, A. V., "Standard Methods of Drying Sultana Grapes in Australia," Pamphlet No. 6, Commonwealth of Australia Council for Scientific and Industrial Research, 1928.
- 15 BUERGER, I. J., "Rack System of Drying Vine Fruits," *Farming in South Africa*, 1930, 5, 309.
- 16 BACK, E. A., "Insect Control in Flour Mills," *U.S. Dept. Agric. Bull.* 872, 1920.
- 17 CHITTENDEN, F. H., and POPENOE, C. H., "Carbon Tetrachloride as a Substitute for Carbon Bisulphide in Fumigation against Insects," *U.S. Dept. Agric. Bur. Ent. Bull.* 96, Part IV., 1911.
- 18 DEAN, G. A., "Heat as a Means of Controlling Mill Insects," *J. Econ. Entomol.*, 1911, 4, 142.
"Further Data on Heat as a Means of Controlling Mill Insects," *J. Econ. Entomol.*, 1913, 6, 40.
- 19 ROARK and COTTON, "Ethylene Oxide as a Fumigant," *Ind. Eng. Chem.*, 1929, 20, 805.
- 20 THOMAS, J. E., "Dried Fruit Grubs : The Ethylene-Dichloride Carbon-Tetrachloride Fumigation Process," *Austral. Journ. Coun. Ind. Res.*, 1929, 2, 128.
"Ethylene Oxide as a New Fumigant for Dried Fruits," *ibid.*, 1931, 4, 53.

- 21 CALDWELL, J. S., "Evaporation of Fruits," U.S. Dept. Agric. Bull. 1141, 1923.
- 22 "Commonwealth of Australia : Development and Migration Commission," Report on the Apple Industry of Tasmania.
- 23 SKIBBE, A., "Sulphuring of Sultanas," *Farming in South Africa*, 1929, 3, 1199.
- 24 CARRIER, W. H., "The Theory of Atmospheric Evaporation, with Special Reference to Compartment Dryers," *J. Ind. Eng. Chem.*, 1921, 13, 432.
- 25 CARRIER, W. H., and STACEY, A. E., "The Compartment Dryer," *J. Ind. Eng. Chem.*, 1921, 13, 438.
- 26 BUTCHER, C. H., "Chemical Engineering Memoranda : 'Drying and Calcining Plant,'" *The Industrial Chemist*, 1927, 3, 554; *ibid.*, 1928, 4, pp. 47, 91, 355.
- 27 CRUESS, W. V., and CHRISTIE, A. W., "A Laboratory Manual of Fruit and Vegetable Products," McGraw-Hill Book Co. Inc., 1922.
- 28 HAUSBRANDT, E., "Drying by Means of Air and Steam," Scott, Greenwood & Son, 1924.
- 29 LEWIS, W. K., "The Rate of Drying of Solid Materials," *J. Ind. Eng. Chem.*, 1921, 13, 427.
- 30 RIDLEY, G. B., "Tunnel Dryers," *J. Ind. Eng. Chem.*, 1921, 13, 453.
- 31 TIEMANN, H. D., "The Theory of Drying and its Application to the New Dry Kiln," U.S. Dept. Agric. Bull. 509, 1917.
- 32 FALK, K. G., FRANKEL E. M., and MCKEE, R. H., "Low Temperature Vacuum Food Dehydration," *J. Ind. Eng. Chem.*, 1919, 11, 1036.
- 33 OWER, E., "Measurement of Air Flow," Chapman & Hall, London, 1927.
- 34 BACK, COTTON and YOUNG, "Ethylene Oxide as a Fumigant for Food and Other Commodities," *J. Econ. Entomol.*, 1930, 23, 226.
- 35 REED, H. M., "Insect Control in Dried Fruits," *Food Industries*, 1931, 3, 117.

PART IV.

CONSIDERATIONS COMMON TO ALL PRESERVED
FRUITS.

CHAPTER XII.

DISCOLORATION IN FRUIT PRODUCTS.

THE colouring matters in plants are of two kinds, viz. those which are soluble in the cell sap, and those which are bound up in an insoluble form in differentiated portions of the protoplasm known as chromoplasts or chloroplasts.

The soluble colours are known as anthocyanins, and include all the blues, purples, violets, mauves, magentas and nearly all the reds. They are concentrated mainly in the epidermal tissues, but may also be found in the interior of the fruit. The insoluble colours which include substances like chlorophyll and carotin form the greens and most of the yellows and oranges. The scarlets, orange-reds, browns and blacks may be due to the presence of both soluble and insoluble colours in the same tissues.

The anthocyanins are widely distributed in plants, and, according to Onslow,¹ their formation is in all probability connected with the formation of sugars, since an increase in the concentration of sugars in a tissue in many cases is accompanied by the development of anthocyanin pigments.

Onslow regarded the group of substances known as flavones as the immediate precursors or chromogens from which the anthocyanins are formed by oxidation, but this view is disputed by other authorities (Everest,² Willstätter,³ Combes⁴), who believe that the direct opposite is the case, viz. that the flavones are produced by oxidation of the anthocyanins. In any case, however, it would seem that either of these groups of substances would be capable of providing the oxygen necessary for corrosion of tin in the presence of organic acids.

The anthocyanins are glucosides readily soluble in water and, as a rule, in alcohol, the solution in the latter being often colourless, or nearly so. They are insoluble in chloroform and ether. When the sugar is split off, as by hydrolysis with dilute acids, the resulting products which are non-glucosidal are known as anthocyanidins. These, in the form of chlorides, are insoluble in ether, but, according to Onslow, are generally soluble in water and alcohol. The anthocyanins may be distinguished from the anthocyanidins by the addition of amyl alcohol, in which the latter are soluble but the former are not.

The anthocyanins turn red in acids, and blue with alkalis. Since, however, they generally occur in nature together with tannins and flavones which turn deep yellow with alkalis, the addition of alkali to most fruit juices gives a green or bluish-green colour.

With zinc dust and hydrochloric acid the colour of an anthocyanin solution disappears, but reappears on standing in air. The colour is also bleached by sulphurous acid, but is restored either by heating to drive off the sulphurous acid or by the addition of a stronger acid.

According to Willstätter, anthocyanin is itself an acid, and in the free state is purple. There is a blue modification, which is the potassium salt of the purple, and a red modification, which is the oxonium salt of anthocyanin. In *Centaurea*, as well as in some other plants, all three forms readily change to a colourless isomer; but with the red form this only occurs in the absence of excess of acid. The change to the colourless isomer can be prevented by adding neutral salts, which form additive compounds with the anthocyanin in solution.

The most important fruits containing anthocyanins are raspberries, strawberries, blackberries, loganberries, cherries, red and black currants, red gooseberries, red, blue or purple plums, damsons, bilberries and cranberries. Greengages, green gooseberries, yellow plums, and apricots and tomatoes, on the other hand, contain insoluble colours. Peaches and many varieties of apples contain anthocyanins, but as these are

mainly in the skins, which are removed in preparing the fruit for canning, the canned material usually has little or no purple colour.

Fruit juices containing anthocyanin often undergo colour changes with metals or the anthocyanin may be precipitated, as when lead acetate is added. It is, however, impossible to say how far the colour changes are due to the presence of impurities like tannins and flavones or to the reaction of the anthocyanin itself. Iron has the effect of turning many fruit juices green or greenish-black; copper also darkens them; aluminium or tin salts turn them violet or mauve; in fact, Shibata and Kasiwagi have shown that the addition of metal to the aqueous solution of a very large number of anthocyanins, extracted from the coloured parts of plants, results in a shifting of the colour to the violet end of the spectrum, the degree of alteration of the colour depending on the metal employed.

Culpepper and Caldwell⁵ have carried out experiments on the behaviour of a large number of fruit juices towards tin and aluminium. Their results confirm those of Shibata, Shibata and Kasiwagi.⁶ They state that the effect of heating anthocyanin-containing materials in a container coated with metallic tin, or in glass in the presence of metallic tin, tin salts, or aluminium salts, is to produce some degree of modification of the original colour towards purple in the case of every material tested, with the exception of those in which the pigment is totally converted to a colourless form under heat. They also noticed in many cases the formation of milky precipitates or suspensions, which they thought to be hydrated stannous oxide.

The purple colours were less evident at high acidity than at low, the presence of excess of acid preventing the combination of the tin with the pigment. By altering the acidity a whole range of colours from red to purple could be obtained. Bleaching of the colour was also noticed after prolonged action by tin, and there was a tendency for the liquid to become turbid and milky, an appearance which Culpepper and Caldwell thought to be due to the formation of hydrated stannous oxide.

Exposure of the bleached liquid to air usually brought about a return to a purple colour, which, however, differed from the original colour of the fruit.* Bleaching was also caused by reduction accompanying the action of fruit acids on the steel base of cans.

Fruits in which a loss of colour is particularly noticeable as the result of heating in glass without metallic contamination are strawberries and cherries, especially if the quantity of pigment is low initially. The colours of these fruits change to a dull brownish-red, which is little affected by subsequent addition of tin; most fruits, however, suffer on prolonged storage, as a comparison of the colours of jams or bottled fruits a year or more old with those of the same varieties, freshly made, will show. Culpepper and Caldwell suggest that the fading may be due to the formation of colourless isomers as observed by Willstätter and his pupils. Kohman thinks that insoluble products may be formed by acid hydrolysis of the anthocyanins, but final proof is lacking for either of these views.

For the effect of anthocyanin pigments on corrosion see under "Spoilage" (p. 131).

Flavones, Tannins, etc.

These have already been mentioned as being generally associated with anthocyanins. They are both widely distributed soluble substances of a pale yellow colour, which changes to a deeper yellow with alkali; tannins are especially abundant in woody tissues, e.g. pips, etc. With iron they take on greenish or greenish-purple tints. Catechol compounds also turn green with ferric salts.

Insoluble Colours.

The yellows are, on the whole, less affected by metals or by heat treatment than the anthocyanin colours. Chlorophyll,

* A development of purple colour on exposure has occasionally caused trouble with canned peaches. This has been traced to anthocyanin pigments derived from the tissues around the stone or from the skins.

however, turns brown after prolonged heating in the presence of acid. Copper forms a deep green colour with chlorophyll, which is stable towards heat. This has led to the addition of traces of copper to colour greengages and many vegetables, a practice which is now prohibited. Zinc also fixes the green colour in canned vegetables.

Contamination with Metals.

The chief sources of contamination with metals are the water, pipes, pans and other utensils used in the various manufacturing processes. The water should therefore be tested to see whether it is free from iron. It should also be softened if hard, since deposits of calcium or magnesium phosphates, oxalates, or other insoluble salts of these metals occasionally cause turbidity in syrups as, for example, in canned or bottled rhubarb, which may have its good appearance destroyed by a deposit of calcium oxalate. No ordinary iron pipes or gutters should be used for conducting any liquids of an acid nature. These should be of stainless steel or other relatively non-corrodible metal, such as German silver or delta metal, and should be thoroughly washed out after use. Filling machines for jam, syruing machines, steam-nozzles and the like are usually made either of phosphor-bronze or monel metal. In evaporators of the climbing or falling-film type, for concentrating fruit juices, all pipes through which the hot juice must pass should be of stainless iron or steel. Tinned copper is unsatisfactory for this purpose, as it is generally found that sufficient of the metals will be dissolved to cause discoloration or give a metallic flavour to the concentrated product.

*Recent work by Bryan and Morris has shown that two parts per million of iron darken strawberry pulp perceptibly, and that discoloration by tin is most serious when anthocyanins are most abundant, as in black currants. The tin is largely precipitated on heating and tends to cause milkiness. Copper and nickel do not cause discoloration so readily, and aluminium is also relatively free from blame in this respect.

Boiling-pans for jam or for making syrup are usually made of copper, which has the advantage of having a low specific heat and being an excellent conductor ; as stated in the jam section, however, it is good practice to have these heavily silvered inside,* although it seems probable that copper received some protection in jam-boiling, possibly from sugars and other substances present, and also because of the fact that air is quickly expelled from the jam by heat. Pans made of stainless steel, nickel, monel metal or aluminium† are also satisfactory for various purposes. Generally speaking, copper, tin and monel metal are only attacked by non-oxidizing organic acids in the presence of air ; stainless steel and aluminium are protected by a film of oxide and are more likely to break down in the absence of air. Aluminium and also nickel are attacked by fruit acids when heated.

A certain amount of contamination with tin and iron when fruits are packed in tin-plate cans is unavoidable, and is shown by the milkiness and purple or dark colours already mentioned. With cans lacquered inside contamination with tin is greatly reduced, especially if two coats of lacquer are given. This question is discussed under the heading of "Corrosion of Tin-plate."

Discoloration from Biological Causes without Metallic Contamination.

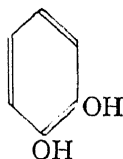
Many fruits undergo more or less rapid browning as the result either of injury or over-ripening ; others do not.

In the former class we have the apple, pear, banana, apricot, peach, cherry, plum, medlar, strawberry, grape ; in the latter, red and black currant, gooseberry, raspberry, loganberry, blackberry, lemon, orange, lime, grape-fruit, pineapple, tomato, melon.

* Silver is not attacked by fruit acids, whether hot or cold, and is therefore exceedingly useful in overcoming special corrosion problems.

† Aluminium is liable to attack by hot fruit acids, but is not attacked in the cold.

According to Onslow, browning through injury involves what is known as an oxidase system, which is a system of enzymes which act upon an aromatic substance containing an orthodihydroxy grouping such as that in catechol. Such substances are widely distributed in plants and include catechol, protocatechinic acid, caffeic acid, etc. The action is also accompanied by secondary induced oxidation of a whole range of phenolic substances including tannins.



The enzymes involved are (1), a peroxidase, which is almost universal in the tissues of the higher plants, and is able to decompose hydrogen peroxide with the formation of active or atomic oxygen; (2) an oxygenase, which can catalyse the autoxidation of the catechol compound.

A plant oxidase is therefore made up of three components :—

- (1) a peroxide ;
- (2) an oxygenase ;
- (3) an aromatic substance with the catechol grouping.

Most of the fruits mentioned above, which show rapid colour changes accompanying death of the tissues through mechanical injury, frost, or the action of chloroform, have been found (Robinson,⁷ Onslow⁸) to contain the oxidase system complete. Those which do not show such changes have been found to lack the second and third members of the system.

Methods of Delaying or Preventing the Activity of the Oxidase System.

It has already been emphasised (Chapter III.) that fruit should be dealt with as rapidly as possible. Mechanical injury

should be avoided, a precaution which is facilitated by picking at the correct stage of ripeness. The oxidase is entirely destroyed by heat ; it is also completely checked in its action by sulphur dioxide, and greatly delayed by storage at temperatures between 32° and 40° F. Freezing the fruit solid also brings the action to a standstill, but rapid browning of those fruits which contain the oxidase system occurs on thawing, owing to the damage to the tissues resulting from the formation of ice.

For reasons which do not seem to be understood, the action may be prevented by a weak brine or sugar syrup. Thus, apple slices remain white when dropped into a 2 per cent. solution of common salt or into a 5 per cent. solution of cane sugar. Strawberries retain their colour when mixed with sugar or covered with a sugar syrup, as in the preliminary treatment for freezing (p. 54) ; also fruit which has been frozen without sugar may be thawed under syrup without immediately turning brown, although browning will occur in course of time.

Discoloration by Sulphur Compounds in Canned Foods.

This form of discoloration is most frequently met with in canned meats or marine products, where it is caused chiefly by sulphides of iron formed by the action of hydrogen sulphide or volatile organic sulphides on the container. Owing to the high acidity of canned fruits, sulphide of iron is not formed in them, but sulphide of tin is sometimes seen as a dark stain in the inside of tins of apricots, and occasionally on strawberries and other fruits. It may be due partly to the sulphur sprays used as fungicides, or to ultramarine or sulphur dioxide in the sugar, or to the natural sulphur of the fruit. The action of sulphur in corrosion has already been discussed ; the stain itself is quite harmless, but is displeasing to the eye, and may cause prejudice. If serious it may be overcome by washing fruits which permit such treatment with very dilute alkali to remove

spray residues, by care in the selection of sugar, or by coating the cans internally with a special lacquer containing traces of zinc oxide.¹⁰

REFERENCES.

DISCOLORATION IN FRUIT PRODUCTS.

- 1 ONSLOW, M. W., "The Principles of Plant Biochemistry," Camb. Univ. Press, 1931.
- 2 EVEREST, A. E., "The Production of Anthocyanins and Anthocyanidins," *Proc. Roy. Soc.*, 1918, B. 90, 251.
- 3 WILLSTÄTTER, R., "Ueber die Farbstoffe der Blüten & Früchte," *Sitz. Ber. A.K. Wiss.*, 1914, 402.
- 4 COMBES, R., "Sur la présence dans les feuilles et dans les fleurs ne formant pas d'anthocyane, de pigments jaunes pouvant être transformés en anthocyane," *C.R. Acad. Sci.*, 1914, 158, 272.
- 5 CULPEPPER, C. W., and CALDWELL, J. S., "Behaviour of Anthocyanin Pigments in Canning," *J. Agric. Res.*, 1927, 35, 107.
- 6 SHIBATA, K., SHIBATA, Y., and KASIWAGI, I., "Studies in Anthocyanins," *J. Amer. Chem. Soc.*, 1919, 41, 208.
- 7 ROBINSON, M., "A Comparison of Certain Oxidising Enzymes of Higher and Lower Plants," *Biochem. Journ.*, 1924, 18, 543.
- 8 ONSLOW, M. W., "Oxidising Enzymes of some Common Fruits," *Biochem. Journ.*, 1920, 14, 541.
- 9 PERKIN, A. G., and EVEREST, A. E., "The Natural Organic Colouring Matters," London, 1918.
- 10 BOHART, G. S., "Special Enamel for Corn Cans," Nat. Cann. Ass., U.S.A., Circ. No. 10L, 1924.

CHAPTER XIII.

VITAMINS IN CANNED AND DRIED FRUITS.

OWING to the enormous growth in the consumption of canned foods of all kinds in recent years, it is of interest to know the effect of the various canning processes—especially heating—on the vitamins. A Report of the Medical Research Council on the Present State of Knowledge of Accessory Food Factors¹ states that, in the absence of any possibility of oxidation, vitamin A in butter-fat withstands a temperature of 120° C. for twelve hours without any great loss, although aeration for four hours at this temperature destroys it almost completely. At 80° C aeration for twelve hours has the same deleterious effect, and even at 37° C. butter exposed to air gradually loses its vitamin, whereas when protected from air under similar conditions it retains it. Oxygen is therefore the factor of prime importance in bringing about the destruction of vitamin A. With regard to the nature and origin of this vitamin it has been shown recently by Moore² and others that the precursor, or parent substance, from which it can be produced in animal tissue is carotene, derived in its turn from carotin, a yellow pigment present in carrots, maize, corn and in smaller quantities in many other vegetable products, including grass.

The report also states that vitamin B does not appear to be susceptible to oxidation by atmospheric oxygen, and, in this respect, differs sharply from vitamins A and C. It is not even affected by exposure to ozone, and resists hydrolysis with

acids. There is no serious destruction of vitamin B by heat with products like bread and cereals if the temperature does not rise above 100°C. , but the report states that tinned foods, such as meats, which are cooked at temperatures above 100° , are liable to contain very little or no vitamin B. Tinned tomatoes, on the other hand, are rich in this vitamin, and the various forms of condensed, evaporated and dried milk contain practically as much of it as fresh milk.

Vitamin C, which is the accessory food factor of most importance in fruits is, like vitamin A, extremely sensitive to oxidising agents, including atmospheric oxygen, especially when the temperature is raised and the hydrogen-ion concentration lowered, whereas in the absence of oxygen it is moderately stable. It has been found that, in some cases, rise of temperature (100° - 200°C.) does not inactivate antiscorbutic materials (fruit juice, hay), whereas oxidising agents more or less rapidly render them devoid of potency. Zilva³ (1922) found that de-citrated lemon juice ($p_{\text{H}} = 6.8$) could be boiled for two hours in an atmosphere of carbon dioxide without loss of potency; whereas in a single hour in a current of air its potency was reduced to less than 25 per cent. of the original. Zilva repeated the experiment with juice at higher acidity, and obtained much less destruction at 100°C. by an air current, hence it is concluded that the susceptibility of the vitamin to oxidation increases as the acidity decreases. Lemon juice made alkaline ($p_{\text{H}} = 12$) lost its potency in twenty-four hours at ordinary temperature, but there was no appreciable loss in the absence of air.

Considerable losses of vitamin C are recorded in cooking cabbage leaves in water, presumably in open vessels. Ninety per cent. of the original antiscorbutic value may be lost in one hour at 80° - 100°C. : even twenty minutes at 90° - 100°C. was sufficient to destroy 80 per cent.

An interesting point emerging from tests on the effect of heating foods containing vitamin C is that the destructive effect of heat is increased only to a slight degree with rise of

temperature over the range employed in cooking, the coefficient of destruction being about 1.5 for each rise of 10° C.⁶

Although an artificial decrease in the acidity of an acid material, like lemon juice, increased the rate of destruction of vitamin C by heat in the presence of air, and although in a non-acid product, like cabbage juice, the vitamin was destroyed more quickly than in lemon juice, it does not follow that the addition of acid to a non-acid product gives protection. In fact, the addition of citric acid, in cooking germinated lentils, caused rather more rapid destruction of vitamin C than when no acid was added. It follows, therefore, that in cooking vegetables there should be no addition either of acid or alkali to the water in which they are boiled.

In summing up the effect of heating on vitamin C, the Report ¹ states that this vitamin is gradually inactivated by rise of temperature in the presence of air at a rate which increases as the H-ion concentration falls, and the rate of inactivation varies with different materials. In the absence of air the rate of inactivation is greatly decreased, but accurate experiments are still lacking as to the exact extent of the change under these conditions. The fact that, over the range of temperature employed in ordinary cooking processes, variation in the temperature employed has a comparatively small influence on the rate of destruction of the antiscorbutic vitamin, renders a short cooking period at a higher temperature preferable to the prolonged cooking at a lower temperature necessary to render the food palatable.

In canning foods it must be remembered that air, except such as may be present in the headspace of the can and in the tissues of the food product, is very largely excluded. If, therefore, the process of exhausting the can before sealing is properly carried out, destruction of the vitamins by oxidation in canning should be reduced to a minimum. There are, thus, reasonable grounds for asserting that most canned foods should contain more vitamin C than fruit cooked in an open vessel. Also, since a rise in temperature does not increase the rate of destruc-

tion of vitamins to the same extent as it increases the velocity of ordinary chemical reactions, it seems likely that the cooking of foodstuffs in cans for a relatively short time at high temperature will not bring about as much destruction of vitamins as is ordinarily found with foods cooked more slowly.

A considerable amount of evidence has been collected,* particularly by Kohman ⁴ and co-workers, to show that canned vegetables and fruits are rich in the various vitamins. Thus, canned spinach is said to be nearly as rich in vitamin A as butter-fat, the vitamin being unaffected by the canning process. It is also rich in vitamin C, in spite of the fact that a large proportion is destroyed in the early stages of cooking. Canned peas are said to be an excellent source of all three vitamins, and canned tomatoes contain A and B, and are particularly rich in C. Kohman also states that "canned cabbage, peas and spinach were shown to be richer in vitamin C than cabbage, peas and spinach respectively purchased on the market and home-cooked by the customary methods," but, although such a statement may generally be correct, there is always the possibility that samples of vegetables collected in this way might show variations quite apart from any difference in cooking. Canned foodstuffs, for instance, usually have the advantage of being in exceedingly good, fresh condition at the time of cooking.

The work of Holst and Frolich ⁵ on cooked cabbage indicates considerable destruction of vitamin C at temperatures above 100° C.; this, however, does not receive complete support from the work of Delf,⁶ in fact it is on her work that the statements previously (p. 224) made in regard to cooking times and temperatures were largely based.

In fruits, whether home-cooked or canned, it has been

* Kohman, E. F. ("Stabilizing Nutrients by Canning," *Ind. and Eng. Chem.*, 1932, 24, 650), quotes an experiment by Eddy in which rats and guinea-pigs have been fed exclusively on canned foods and have reached the fifth and seventh generation in optimum condition as regards growth, lactation and reproduction without exposure to direct sunlight or ultra-violet radiation.

shown by Kohman and others that the acidity gives considerable protection to vitamin C. Kohman states, however, that apples used "in baking, in making apple sauce and in canning by the ordinary procedure" lost all their vitamin C. This is ascribed to the presence of much oxygen in the tissue of the apple, and it is claimed that soaking in weak brine (see p. 85) for twenty-four hours before cooking, allows time for this oxygen to be removed in respiration so that subsequent heating in canning does not destroy the vitamin. In contrast with this must be placed the work of Bracewell, Hoyle and Zilva,⁷ who have baked apples (Bramley's Seedling)* in their skins in a hot-air oven at 115° C. for about fifty minutes, with very little or no loss of vitamin C. During this time observation was made on the temperature of the apple by introducing a thermometer into the tissue to the depth of the core. The temperature rose from about 25° C. after five minutes to about 95° C. at the end of the heating. Some research would appear necessary to reconcile the findings of these workers, but in any case, the work of Zilva has shown that apples vary very greatly in their content of vitamin C, and that the peel and the tissues just below it are by far the richest part of the fruit. The introduction of juice from the peelings in canning apples might, therefore, be well worth considering, since, without such juice, much vitamin is lost whatever method of canning is adopted.

Vitamins in Jams.

Very little research has been carried out on the vitamin content of jams; naturally much would depend on the treatment and condition of the fruit before boiling. One test on marmalade has shown it to be very low in vitamin C; but, in any case, the function of such products is rather to render other foods palatable than to act as food in themselves, although, of course, they contain valuable sugars, fruit acids, etc.

* Zilva and co-workers found this variety richer in vitamin C than any other commercial cooking apple tested by them. Several varieties gave relatively little protection from scurvy.

Vitamins in Dried Fruits.

Dried fruits appear to vary considerably in their vitamin content, owing probably to the conditions of drying and the period of storage. It has been shown that prolonged exposure to air and light destroys vitamin A, even in butter-fat, and this is certainly true of other materials like hay and dried vegetables. Tests with dried tomatoes have shown that these still contain all three vitamins, although there was less vitamin C than in canned tomatoes. Dried lemon and orange juice still contained abundance of vitamin C. Hess and Unger⁸ in 1918 found no antiscorbutic properties in dried prunes, but no details were given of the method of drying, and no comparison was made with fresh prunes from the same orchard. Morgan and Field,⁹ and Morgan, Field and Nichols,¹⁰ studied the effect of the treatment (dipping and sulphuring) of peaches, apricots and prunes before drying on the retention of the antiscorbutic vitamin, and also compared the same fruits sun-dried and dehydrated. They found with apricots and peaches that, if 450-500 or more parts of sulphur dioxide per million were retained, sulphuring protected vitamin C from destruction, whether the fruit was sun-dried or dehydrated. With prunes this protection was greatest when the fruit had been dipped in boiling lye, owing to the fact that the lye treatment facilitated the penetration of the fruit tissues by the sulphur fumes. They also found that artificially dehydrated prunes had greater antiscorbutic value than those which had been sun-dried. In the work the tests were comparable since, as far as possible, this fruit was gathered at the same time from the same orchard and control experiments on fresh or frozen samples were carried out. In this connection it was observed that apricots frozen in the presence of air lost their vitamin, but that it was not destroyed when the air was removed before freezing.

Morgan, Field and Nichols compare their results with those of Williams and Corran (p. 58), who found that lemon juice stored in a sulphured cask retained its vitamin, sulphuring being preferable to the addition of a metabisulphite which afforded no protection.

Effect of Storage on Canned Products.

The evidence on this subject is somewhat meagre, but, so far as it goes, it tends to show that there is little or no destruction of vitamins during storage of canned fruits.

Conclusion.

Taking the question of the vitamin contents of these classes of foods as a whole, there still seems room for a great deal of critical work, especially in regard to comparisons between canned or dried foods with the same foods from the same farm in fresh condition or cooked in other ways. At the same time, it seems clear that a number of canned products, notably canned tomatoes, are valuable sources of vitamins, and there is no reason at all why other canned fruits should be less potent than those cooked in the ordinary way: they ought, indeed, to be more potent, since the cooking temperatures in canning fruits do not exceed 100° C., and air is excluded. The same statement should also apply to products, such as vegetables and meats, when canned under the best conditions and according to the best methods, although higher temperatures are employed for these. Where results have been obtained which point to the opposite conclusion, it is possible to suggest that in all probability the best conditions have not been observed.

Note.—Remarks which apply to vitamin A also apply to the antirachitic vitamin D, since these are closely associated. The antisterility vitamin E has been very little studied so far, but such evidence as is available points to the fact that it is more stable towards heat than any of the other vitamins dealt with here.

REFERENCES.

VITAMINS.

- 1 Report of the Medical Research Council on the Present State of Knowledge of Accessory Food Factors (1924, reprinted 1927).
2. MOORE, T., *Biochem. J.*, 1932, 26, 1, and previous issues.
- 3 ZILVA, S. S., *Lancet*, 1922, 1, 1243.
Biochem. Journ., 1922, 16, 42.

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- 4 KOHMAN, E. F., "Vitamins in Canned Foods," Bull. 19L, Res. Lab., Nat. Cannery Assn., Washington, D.C., 1927.
- 5 HOLST, A., and FROLICH, T., 7, *Hyg.*, 1907, 7, 634; *ibid.*, 1912, 72, 1.
- 6 DELF, E. M., *Biochem. Journ.*, 1918, 12, 416; *ibid.*, 1920, 14, 211.
Publications of South African Inst. Med. Res. No. XIV., Johannesburg.
- 7 BRACEWELL, M. F., HOYLE, E., and ZILVA, S. S., "The Antiscorbutic Vitamin in Apples," Spec. Rep. Med. Res. Council No. 146, 1930.
- 8 HESS, A. F., and UNGER, L. J., *J. Biol. Chem.*, 1918, 35, 479 and 487.
- 9 MORGAN, A. E., and FIELD, A., "The Effect of Drying and of Sulphur Dioxide upon the Antiscorbutic Property of Fruits," *J. Biol. Chem.*, 1929, 82, 579; 1930, 88, 9.
- 10 MORGAN, A. E., FIELD, A., and NICHOLS, P. F., "The Effect of Drying and Sulphuring on the Vitamin C Content of Prunes and Apricots," *J. Agric. Res.*, 1931, 42, 35.

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